BUDAPEST UNIVERSITY OF TECHNOLOGY AND ECONOMICS
FACULTY OF MECHANICAL ENGINEERING
DEPARTMENT OF POLYMER ENGINEERING

ANALYSIS OF COLOR INHOMOGENEITY IN MASTERBATCH COLORED INJECTION MOLDED PARTS

THESIS BOOK OF PHD DISSERTATION

WRITTEN BY:
LÁSZLÓ ZSÍROS
MSC. IN CHEMICAL ENGINEERING

SUPERVISOR:
DR. JÓZSEF GÁBOR KOVÁCS

2019

The review and the defense report of the doctoral dissertation can be viewed at the Dean's Office of the Faculty of Mechanical Engineering of the Budapest University of Technology and Economics

1. Introduction

Nowadays the two most important plastic processing technologies are the extrusion and the injection molding. If we look at it from the processed amount point of view, the two technologies are very close to each other, but if we consider the number of products, then the amount of injection molded goods is far above the extruded products. This is because of the injection molded products are much more diversified from design point of view than the extruded products. The continuously growing number of injection molding applications demands a very high quality both from mechanical and from aesthetical perspectives as well. If colored injection molded parts have to be produced, there are three options to choose from.

The first is production from previously colored material, called precolored material, where the material has been colored in a separated technological step prior to injection molding such as compounding, so in the injection molding step it is not needed to mix anything into the polymer. In this case the material used for injection molding has exactly the same color as our injection molded parts, and the parts have a very good color homogeneity. In case of applications where the quality requirements are very high both from functional and aesthetical and safety point of view, usually this technology is chosen from the available options. This option is very comfortable from processing point of view as well, since this coloring technology does not require additional equipment, or modification on the machines in the injection molding factory, so the investment cost of a new factory is relatively low in this case, and it is not required to have high qualified and experienced employees in the factory, although it is a big disadvantage, that the raw material costs in case of pre-colored material is much higher (approximately 20-70%) compared to the production from raw material and masterbatch.

The second option is to color the material by masterbatch. In this case the coloring of the nature material takes place in the injection molding machine by the masterbatch pellets. The two main components of the masterbatch pellets are the carrier, and the coloring agents, such as dyes and pigments, which are small molecule organic or inorganic materials. If the production is cost sensitive, this technology would be chosen. Altogether 90% of the manufacturers are using masterbatches for coloring the raw material, since the price of the raw material can be decreased substantially. In this case the investment cost of building a new factory is fairly higher, but the return on investment (ROI) time of the additional equipment is very short if the factory is running continuously. The factory will also need higher qualified and more experienced employees for dealing with the technological challenges, but from cost perspective it is not important since in the total production cost of an injection molded part, the cost of human resources is usually less than 10%. Therefore, the increase of a 10-20% cost on human resources results only 1-2% increase in the total production costs, what is a minor increment compared to the precolored material costs. However, the result of applying this technology is usually that the parts sometimes have color inhomogeneities, what can be detected visually as well. In cases of certain colors and polymers it can be a huge challenge for the factory to produce high quality parts continuously.

In the third option the coloring of the raw material also takes place in the injection molding machine, but instead of the solid masterbatch pellets, the colorant material is a liquid. This liquid also consists of a carrier (what is liquid in this case, such as mineral oil, PIB, liquid sliding agents) and different coloring pigments and dyes. This technology is usually applied if only small amount of materials has to be colored, because in this case masterbatches cannot be used in an economically reasonable way.

Based on the fact that most of the injection molded parts are colored by different masterbatches, this work focuses on the challenges of this coloring technique. For the evaluation of the changes in the technology, such as the application of different mixing equipment and technological parameter changes, it is necessary to have a measurement system, which is precise enough, and has a good repeatability and reproducibility. Such a measuring system has not existed before, therefore the first and most important step of this work was to establish and validate a measurement system. With this system different aspects of the masterbatches and the masterbatch using coloring technology were investigated.

2. The review and critical analysis of the literature

The color inhomogeneities in the past usually has been evaluated visually by a board of professionals giving points typically from 1 to 10, but this method has several disadvantages: the ability of the reproduction of a measurement is uncertain, and the measurement results have high standard deviation, what makes impossible to decide if a change in the average value is significant. This measurement method is simply unable to show the differences between most of the mixing equipment. Therefore, it is clear that there is a need for setting up an automated measurement method what is in line with human judgments but has better repeatability and lower standard deviation. Automated measurements have another advantage as well over the human judgments: the measurement itself needs much less time.

Based on the literature review it can be stated that an automated measurement system, which works with significantly lower standard deviations, could be a step forward in this field and could make it possible to investigate such phenomena which were not possible by human evaluations. Having such a system, an experimental homogenization test could be executed with different mixing equipment, which is currently missing from the literature. However, some numerical studies are available for static mixers, they are not available for dynamic mixers at all due to their extreme complexity. Furthermore, the effect of different injection molding parameters could be cleared as well, since conflicting results are observed. By the introduction of a standardized homogeneity measurement of masterbatches estimations could be made on a certain injection molding setup for the inhomogeneity level of the molded parts. This could be a definite improvement in the field of engineering the mixing efficiency of injection molding machines, and developing better masterbatch receipts, and the role of injection mold design could also be mapped by using a novel objective measurement method.

By knowing the scientific background of this field, my dissertation has the following aims:

- the development of a measurement method, which can be used as a standard for quantitative measurement and comparison of the effect of different equipment and parameters on the color inhomogeneity of injection molded parts,
- the quantitative comparison of the effect of static and dynamic mixers on color inhomogeneity in case of injection molded parts,
- the measurement of the effect of processing parameters on color inhomogeneity in case of injection molded parts,
- the analysis of the effect of static mixer diameter and element number on the color inhomogeneity,
- the characterization of the masterbatch receipts based on their homogenization properties,
- the analysis of the effect of mold design on perceived color inhomogeneity.

3. The materials and machines used for the tests

In the following chapters I present the equipment, materials and test methods used and applied in this work.

3.1. Injection molding materials

All investigations have been carried out with ABS Terluran GP35 raw material. There were two main types of masterbatches used and tested: commercially available masterbatches and the ones specifically manufactured for the tests. Generally, it can be stated that all these masterbatches were formulated on ABS carrier by one of the leading masterbatch manufacturing companies such as Clariant, PolyOne and A. Schulman. The used colorants in the specifically formulated masterbatches are represented in Table 1. The tests regarding the effects from the masterbatch compositions were designed together with the representants of the above mentioned companies.

Sample no.	Name	Raw material	Supplier
1	Red dye	Macrolex Red EG – CI Solvent Red 135 – perinone	Lanxess
2	Red O	Cinilex DPP Red SR2P – CI Solvent Red 254 – diketopyrrolopyrrole	Cinic
3	Red Mono 1	In-house produced by the manufacturer	A Schulman
4	Red Mono 2	Microlen Red 2030-MC – CI Solvent Red 254 – diketopyrrolopyrrole	BASF
5	Red IO	Bayferrox 130 – CI Pigment Red 101 – iron oxide	Bayer
6	Blue dye	Keyplast Blue FR – CI Solvent Blue 104 - anthraquinone	Keystone
7	Blue O	Heliogen K 6902 – CI Pigment Blue 15:1 – copper phthalocyanine	BASF
8	Blue Mono	Eupolen PE Blue 69–2001- CI Pigment Blue 15:1 – copper phthalocyanine	BASF
9	Blue IO	NI-12 UM Blue – CI Pigment Blue 29 – Ultramarine blue	Nubiola

Table 1. Colorants used in the specifically manufactured masterbatches

3.2. Mold and machines

A special injection mold was developed to execute the investigations. The mold can produce 80 mm by 80 mm flat specimens with variable wall thickness. The cavity inserts can be exchanged to alter the surface roughness, and the gate inserts can also be changed to study the effects from various gate types such as the pin gate, film gate, multiple pin gates and a modified film gate. The injection mold and its inserts are illustrated on Figure 1.

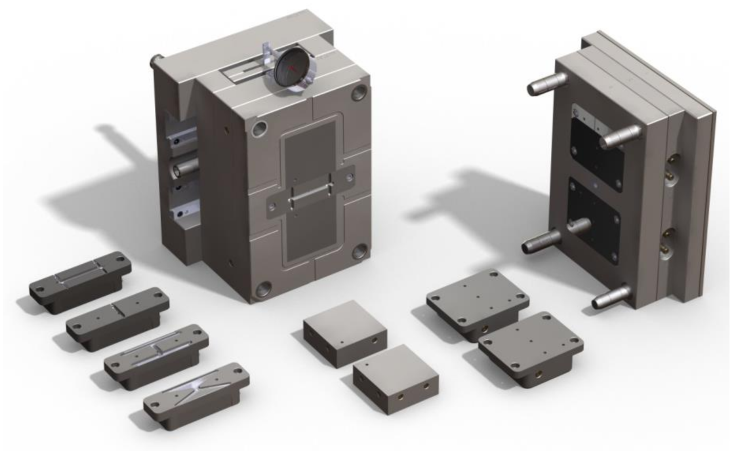

Figure 1. The injection mold with the exchangeable inserts used for the tests

Injection molding machine Arburg Allrounder Advance 370S 700-290 type (screw diameter 30 mm) was used for the tests. The injection molding parameters used in the tests can be seen in Table 2. In the test series where the effect of the injection molding parameters were tested the injection rate, the pause time and the barrel temperature were altered to a higher and a lower value compared to the parameters indicated in Table 2.

Injection molding parameter	Value
Volume [cm^3]	50
Injection rate [cm^3/s]	55
Injection pressure [bar]	various
Switch-over point [cm^3]	altered
Holding pressure [bar]	600
Holding time [s]	6
Residual cooling time [s]	11
Pause time [s]	0
Screw rotational speed [m/min]	25
Backpressure [bar]	60
Decompression volume [cm^3]	6
Decompression rate [cm^3/s]	20
Barrel temperature [°C]	225
Mold temperature [°C]	40
Cycle time [s]	22.6

Table 2. Injection molding parameters

3.3. Measurement method development

The steps of the measurement method can be seen in Figure 2. In the preparation step, the raw material was dried and mixed with masterbatch in the prescribed ratio (4% in most of the cases). Test specimens were injection molded with the machine and mold using the parameters described in chapter 3.2. For the digitization of the samples an HP Scanjet G4010 and an EPSON Perfection V 600 Photo have been used. The samples were digitized in 200 DPI resolution. Lower resolution images were inaccurate, while higher resolution images produced almost the same results but calculation time increased drastically. It was investigated and proved that with the proper calibration both scanners could provide comparable results. The raw digitized images needed certain preparations before the evaluation algorithm could be executed on them, since the samples contained ejector marks and some black spots, which could deteriorate the evaluation, and were not in the scope of this investigation series. After the preparation of these digitized images, a special, own developed algorithm has evaluated the samples. The flowchart of the measurement is represented in Figure 2. The algorithm first converts the images which were recorded in RGB color system to CIELAB color system. This is necessary if good correlation with human evaluation is aimed. The first generation of the evaluation software can be seen in Figure 3.

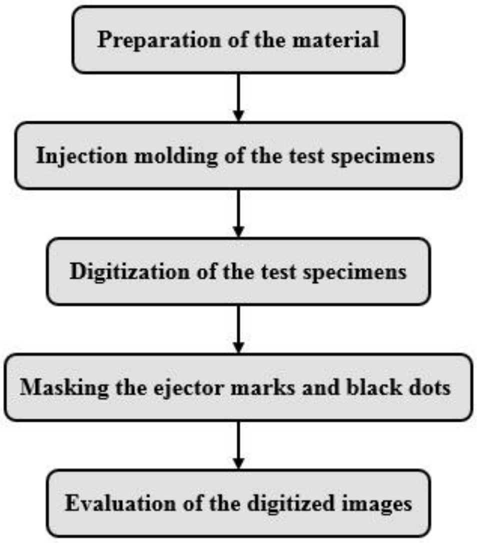

Figure 2. The flowchart of the measurement method

Using the calculated Lab values of the pixels, a moving window scans the picture, and at every (i, j) position of this window the mean color coordinates are calculated ($\overline{a}_{i,j,k}$), where k is the size of the window (Figure 4).

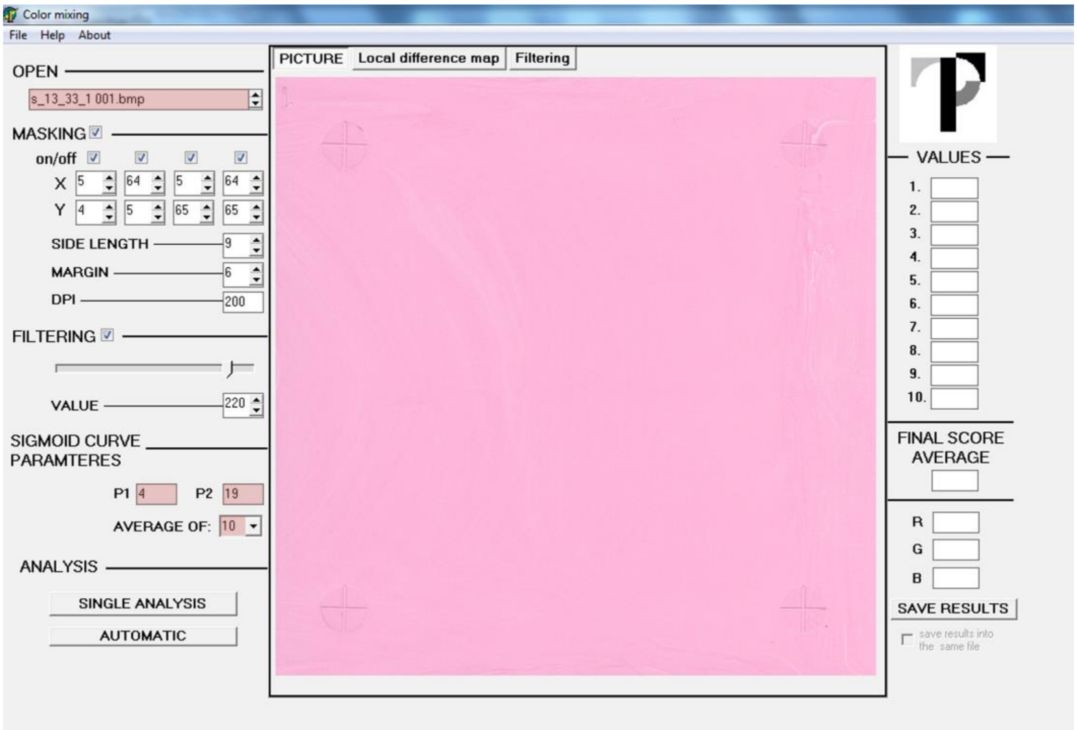

Figure 3. The first version of the evaluation software

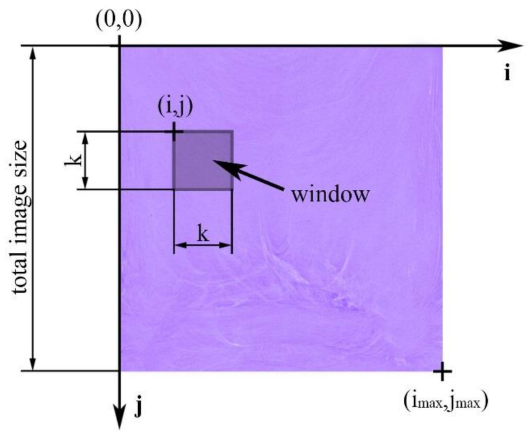

Figure 4. The moving window on the image

The window size (k) could be varied from 1 to the maximum size of the picture. A matrix can be generated from the mean color coordinates as follows (Eq. 1-3):

$$\overline{A}_{i,j,1} = \begin{bmatrix} \overline{a}_{0,0,1} & \overline{a}_{1,0,1} & \cdots & \overline{a}_{i,0,1} \\ \overline{a}_{0,1,1} & \overline{a}_{1,1,1} & & \overline{a}_{i,1,1} \\ \vdots & & \ddots & \vdots \\ \overline{a}_{0,j,1} & \overline{a}_{1,j,1} & \cdots & \overline{a}_{i,j,1} \end{bmatrix}, \quad (1)$$

$$\overline{A}_{i,j,2} = \begin{bmatrix} \overline{a}_{0,0,2} & \overline{a}_{1,0,2} & \cdots & \overline{a}_{i-1,0,2} & n.a. \\ \overline{a}_{0,1,2} & \overline{a}_{1,1,2} & & \overline{a}_{i-1,1,2} & n.a. \\ \vdots & & \ddots & & \vdots \\ \overline{a}_{0,j-1,2} & \overline{a}_{1,j-1,2} & & \overline{a}_{i-1,j-1,2} & n.a. \\ n.a. & n.a. & \cdots & n.a. & n.a. \end{bmatrix}, \quad (2)$$

$$\overline{A}_{i,j,k} = \begin{bmatrix} \overline{a}_{0,0,k} & n.a. & \cdots & n.a. \\ n.a. & n.a. & & n.a. \\ \vdots & & \ddots & \vdots \\ n.a. & n.a. & \cdots & n.a. \end{bmatrix}, \quad (3)$$

where the elements of the matrix can be calculated as follows (Eq. 4):

$$\overline{a}_{i,j,k} = \frac{\sum_{x=i}^{i+k-1} \sum_{y=j}^{j+k-1} P[L,a,b](x,y)}{k^2}, \quad (4)$$

where i and j are the position of the moving window within the whole picture, k is the width and height of the moving window, and x and y are the local coordinates within the moving window.

For all window sizes and positions, the Euclidean distance of each pixel from the mean color coordinates ($\overline{a}_{i,j,k}$) in the given window were calculated. For each window, the average Euclidean distance has been calculated by Eq. (5).

$$MD_{i,j,k} = \frac{\sum_{x=i}^{i+k-1} \sum_{y=j}^{j+k-1} \sqrt{\sum_{\varepsilon=L,a,b} \{P[\varepsilon](x,y) - A[\varepsilon](x,y)\}^2}}{k^2}. \quad (5)$$

In the Lab color space, the distance of two colors are independent from the reference white, therefore it was not necessary to measure that. However, it is possible to execute these calculations in case of $k = 1$, it has no practical importance since in this case all the calculated *MDi,j,k* values are going to equal to zero. In case of $k \geq 2$ values, the lower the $MD_{i,j,k}$ value is, the more even the color of the sample in the area covered by the moving window is. Moving the window pixel by pixel, the software can locate the area having the highest MD_k value which is called HMD_k. If the size of the moving window is equal to the image size in pixels, a global *MD* value (*GMD*) can be obtained. The software calculates the HMD_k values for different window sizes which can be compared to human evaluations.

We asked six color technicians to evaluate the homogeneity of the samples that were used for the calibration of the software we developed. Three of these individuals worked in Hungary and three in Denmark for an international injection molding company in a color technician or quality assurance position and all have at least 2 years of related experience. Three of them were males and the other three were females. Their job included examining the visual appearance of injection molded samples similar to the ones in our tests, in shape, material and size with special attention to color inhomogeneity. The tests were conducted in the laboratory at the company, where the specimens were examined in a SpectraLight QC lightbox, in D65 lighting, from a distance of 30–40 cm, perpendicular to the samples. For the scoring the technicians were only given instructions to rate the specimens on a scale from 0 to 10, in which 0 means visibly homogeneous and 10 means extremely inhomogeneous. Based on these instructions, the technicians considered a sample without stripes and looking homogeneous as faultless (0 points), while strongly striped specimens, which were unacceptable by all standards, were given 10 points.

The reference tests from precolored material showed a small, but consistent color inhomogeneity which was derived from the scanning process. These small color inhomogeneities from the precolored materials were varying with the different colors. These values correlated well to the color inhomogeneity values calculated for the maximum pixel size window (*GMD*) of the masterbatch colored samples. Therefore, *HMD* values have been corrected with *GMD* values to enable the comparison of different colors regarding color inhomogeneity values. By depicting the corrected software scores (*CMD*=*HMD*-*GMD*) against the human scores (Figure 5) it can be stated, that a good correlation does exist, however it is not linear. In Figure 5 CMD values have been calculated for 35 pixel window size, because the correlation showed a maximum at this location (R=0.86).

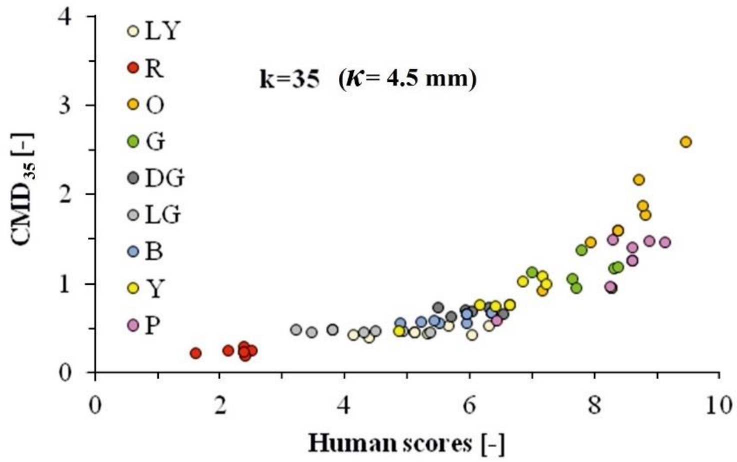

Figure 5. The corrected software scores (CMD) of each color as a function of human scores

Since according to the Weber-Fechner law human perceptions are generally proportional to the logarithm of the stimuli, a logarithmic transformation was applied to the CMD values. The log(CMD) values correlation curve peaked at around 34-35 pixel window size with a maximum value of R=0.95. In Figure 6 the *IHS* (inhomogeneity scores), which are linear transformation of the logarithmic corrected values, have been drawn as a function of the human scores. This linear transformation is represented in Eq. 6.

$$IHS = C_1(log(CMD) + C_2). \quad (6)$$

The constants C_1 and C_2 didn't have any effects on the correlation values. The aim of these constants was only to pull the *IHS* values to a similar scale as the human scores.

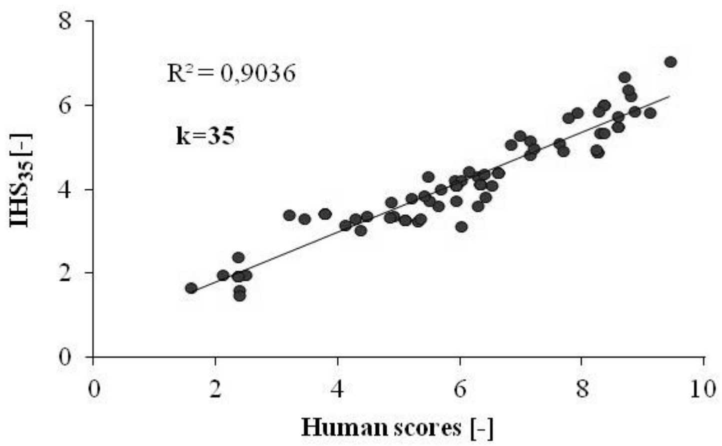

Figure 6. The correlation of the human scores and the logarithm of the corrected software scores at 35 pixel window size

4. Summary

I have developed a novel measurement method to objectively evaluate the color inhomogeneities. The measurement method was performed as follows: 80 x 80 mm injection molded test specimens were produced from ABS GP 35 mixed with various solid phase masterbatches. The test specimens were digitalized by a flatbed scanner, and the images have been evaluated by a software. The software is using a special, own developed algorithm to evaluate the images. It scans the image pixel by pixel with a defined window size and calculates the average Euclidean color difference of the pixels within the window. When the whole image is scanned the inhomogeneity level of the sample is calculated from the highest average Euclidean color difference calculated during the scanning. Furthermore, the average Euclidean color difference is calculated for the whole image as well. While the result from the defined window size is relevant from inhomogeneity point of view, the result of the whole image is typical to the evaluated color and is needed for the correction of the inhomogeneity level to be able to compare the inhomogeneity levels derived from different color shaded masterbatches. I have measured test specimen series with different window sizes, and inhomogeneity scores have been calculated with and without correction and with logarithmic transformation as well. The results have been correlated to human visual inspections, and it has been found that the correlation was the best when the results were corrected with the whole image values with logarithmic transformation. The correlation maximum was more than 95% at 35 pixels window size (200 DPI, κ = 4.5 mm).

This measurement method has been applied to evaluate differences in homogeneity level caused by various injection molding parameters such as the injection speed, the barrel temperature and the residence time of the plastic material in the barrel. It has been shown that increasing of injection speed decreases, while increasing of barrel temperature increases the measured color inhomogeneity. It was also proved as well that the residence time of the material in the barrel had no significant effect on the color inhomogeneity.

I have measured the mixing efficiency of different static and dynamic mixers, and I have shown that there are significant differences in their homogenization capabilities. I have proved that in case of polymer melts colored by solid phase masterbatches numerical approximations of the mixing efficiency leads to wrong conclusions since they are not able to take into consideration the effects from dispersive mixing capabilities of a certain mixer. I have measured several different diameter and element number StaMixCo static mixers and concluded that the mixing efficiency of the static mixer is dependent on its diameter, which is in opposition with the numerical studies from the literature. I have objectively measured and compared the mixing efficiency of dynamic mixers to static mixers which was not possible by numerical studies due to their extreme complexity. I have shown that knowing the boundary conditions, the element number and the diameter of the applied static mixer can be optimized for the maximum homogenization capability. The same measurement method could be applied to differently designed dynamic mixers, to determine which of the design principles are more and less important from homogenization point of view.

I have shown that the different masterbatch compositions had a significant effect on the inhomogeneity of the injection molded products. I have measured the homogenization properties of nine different masterbatches and showed that the qualification of these masterbatches is possible with this measurement system, which significantly improves the possibilities of the development of masterbatch receipts for better homogenization. From the measurements of the different masterbatch receipts it had to be concluded that the primary driver of the inhomogeneity is the interactions between the different components and not the individual properties of the components. I have experienced consequently better results in masterbatch formulations based on organic pigments. Furthermore, the higher amounts of the applied wetting agent in these organic based recipes caused significant improvement in the homogeneity level as well.

I have measured that mold design and surface structure of the product had significant effect on the perceived color inhomogeneity. I have measured these effects in a special injection mold in which the gate inserts and the surface inserts were exchangeable. Generally, it can be stated that gate designs which produced higher shear during the filling improved the color homogeneity, however this phenomenon was distorted by some other factors. The measurements with inserts of different surface roughness showed that the perceived color inhomogeneity is inversely proportional to the logarithm of the surface roughness.

5. Theses

Thesis 1

I have developed a novel measurement method for the quantitative analysis of color inhomogeneity. I have proved that the correlation between the results of the measurement method and human evaluation is higher than 95 %, and the standard deviation of the measurement is one order of magnitude lower than the standard deviation of human evaluation. I have also proved that the standard deviation of the results produced by my method is significantly smaller than the standard deviation of the injection molding process. Therefore, my measurement method is suitable for investigating processes influencing color inhomogeneity during injection molding. For my investigations, I used the results of a group of 6 randomly chosen trained technicians, consisting of 3 males and 3 females. I conducted my experiments on injection molded test specimens made from ABS, Styrolution Terluran® GP-35, mixed with solid phase masterbatches. [1, 2, 8]

Thesis 2

I have proved that my measurement method can be used to quantitatively measure and compare the homogenization capabilities of static and dynamic mixers used in injection molding, and to optimize mixer designs. I carried out the experiments on an Arburg 370S 700-290 injection molding machine equipped with a 30 mm screw. The test specimens were injection molded from ABS, Styrolution Terluran® GP-35, mixed with solid phase masterbatches. [3, 4, 5, 8]

Thesis 3

I have proved that out of injection molding parameters, injection speed and barrel temperature have a significant effect on color inhomogeneity in the case of masterbatches with TiO_2 and dye content. I have proved that increasing injection speed decreases, while increasing barrel temperature increases color inhomogeneity, which is in connection with the increasing shear when injection speed increases and barrel temperature decreases. The tests were performed on test specimens injection molded from ABS, Styrolution Terluran® GP-35, mixed with solid phase masterbatches. [2, 8]

Thesis 4

I have proved with my measurement method that the mixing efficiency of static mixers depends both on the diameter of the mixer and the number of applied mixing elements. This can be explained with the differences in the generated shear in the different static mixers. I have proved that the effect of the static mixers on color inhomogeneity can be described with the following equation: $\Delta IH = K \cdot n$, where ΔIH is the change in inhomogeneity, K is the effect of one element, which depends on the diameter and the geometry of the element, and n is the number of elements. With the help of this and the boundary conditions, the mixing efficiency of a static mixer can be calculated and planned. I have shown that my measurement method enables the optimization of the diameter and the element number of static mixers. I performed my measurements with StaMixCo SMN type mixers with 5, 7 and 8 elements, and diameters of Ø18, Ø22, Ø27 mm. The test specimens were injection molded from ABS, Styrolution Terluran® GP-35, mixed with solid phase masterbatches. [4, 8]

Thesis 5

a.) I have proved that the homogenization properties of different masterbatch receipts are significantly different, and I have shown that these differences can be quantitatively measured with my measurement method. This enables the comparison and rating of different masterbatches based on their homogenization properties. [8, 9]

b.) I have proved that the homogenization properties of solid phase masterbatches primarily depend on the interactions of the components of the masterbatch. I have also shown that the color homogeneity of the individual components cannot explain the differences measured in various injection molded parts colored with a solid phase masterbatch. [7, 8, 9]

Thesis 6

I have shown that perceived color inhomogeneity is inversely proportional to the logarithm of surface roughness. I performed my measurements on test specimens injection molded in a mold with exchangeable inserts of different surface roughness. The test specimens were injection molded from ABS, Styrolution Terluran® GP-35, mixed with solid phase masterbatches. [6,8]

6. Publications

1. **Zsíros L**., Kovács J. G.: Measuring color inhomogeneity of injection molded parts. in ‘Proceedings of OGÉT, Arad, Romania’ 454-457 (2013).
2. **Zsíros L**., Suplicz A., Romhány G., Tábi T., Kovács J. G.: Development of a novel color inhomogeneity test method for injection molded parts. Polymer Testing, **37**, 112-116 (2014).
3. **Zsíros L**., Kovács J. G.: Fröccsöntőgépek homogenizáló képességének optimalizálása. Műanyag és Gumi, **50**, 347-350 (2013).

4. Török D., **Zsíros L**., Kovács J. G.: Különböző elemszámú és átmérőjű StaMixCo statikus keverők vizsgálata. Műanyag és Gumi, **51**, 346-351 (2014).

5. **Zsíros L**., Török D., Kovács J. G.: Development of a color inhomogeneity measurement method and its application to the evaluation of static mixers. in 'Proceedings of OGÉT, Csíksomlyó, Romania' 415-418 (2015).

6. Török D., **Zsíros L.**, Kovács J. G.: Effects of gate type and surface roughness of mold cavity on color homogeneity of injection molded part s. in 'Proceedings of OGÉT, Déva, Romania', (2016).

7. **Zsíros L.**, Török D., Kovács J. G.: The effect of masterbatch recipes on the homogenization properties of injection molded parts. International Journal of Polymer Science, **2017**, 1-7 (2017).

8. **Zsíros L.**, Kovács J. G.: Surface homogeneity of injection molded parts. Periodica Polytechnica, **62**(4), 284-291 (2018).

9. **Zsíros L.**, Török D., Kovács J. G.: Evaluation of the homogenization properties of masterbatches. Coloration Technology, **133**, 431-438 (2017).

10. Morten Hannemose, Jannik Boll Nielsen, **László Zsíros**, and Henrik Aanaes, An image-based method for objectively assessing injection moulded plastic quality. SCIA (2017).