Macro-dispersion Evaluation in Filled Elastomers

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Diplomová práce
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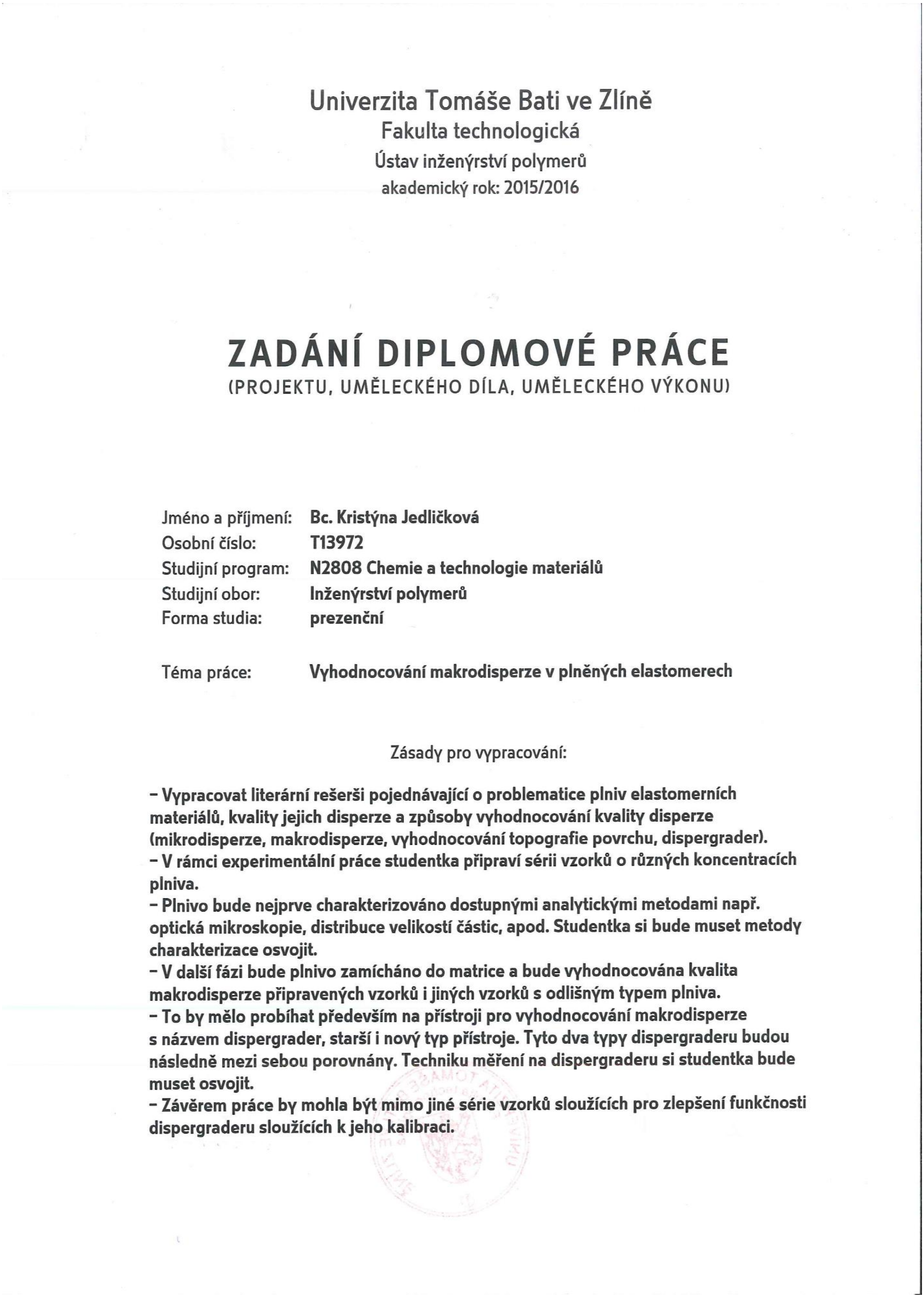
Univerzita Tomáše Bati ve Zlíně
Fakulta technologická



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Ústav inženýrství polymerů
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ZADÁNÍ DIPLOMOVÉ PRÁCE
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Jméno a příjmení:	**Bc. Kristýna Jedličková**
Osobní číslo:	**T13972**
Studijní program:	**N2808 Chemie a technologie materiálů**
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Forma studia:	**prezenční**
Téma práce:	**Vyhodnocování makrodisperze v plněných elastomerech**

Zásady pro vypracování:

– Vypracovat literární rešerši pojednávající o problematice plniv elastomerních materiálů, kvality jejich disperze a způsoby vyhodnocování kvality disperze (mikrodisperze, makrodisperze, vyhodnocování topografie povrchu, dispergrader).
– V rámci experimentální práce studentka připraví sérii vzorků o různých koncentracích plniva.
– Plnivo bude nejprve charakterizováno dostupnými analytickými metodami např. optická mikroskopie, distribuce velikostí částic, apod. Studentka si bude muset metody charakterizace osvojit.
– V další fázi bude plnivo zamícháno do matrice a bude vyhodnocována kvalita makrodisperze připravených vzorků i jiných vzorků s odlišným typem plniva.
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Rozsah diplomové práce:
Rozsah příloh:
Forma zpracování diplomové práce: **tištěná/elektronická**

Seznam odborné literatury:

G. Parfitt. Dispersion of Powders in Liquids: With Special Reference to Pigments. 2nd Ed. London: Applied Science Publ. 1973. ISBN 0-85334-533-3.
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A. Limper. Mixing of rubber compounds. Munich: Hanser Publishers 2012; 239p. ISBN 978-3-446-41743-4.

Vedoucí diplomové práce:	**doc. Ing. Roman Čermák, Ph.D.** Ústav inženýrství polymerů
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Termín odevzdání diplomové práce:	**16. května 2016**

Ve Zlíně dne 1. března 2016

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ABSTRAKT

Tato diplomová práce se zabývá vyhodnocováním makrodisperze v plněných elastomerech. Teoretická část popisuje elastomery, ztužující plniva, míchácí proces, disperze a jako nejdůležitější část řeší metody k vyhodnocování makrodisperze.

Experimentální část zahrnuje měření na přístroji Dispergrader, což je optický mikroskop fungující v odrazovém módu. Hlavní cíle diplomové práce jsou sledování distribuce měřených hodnot pro elastomerní směsi plněné sazemi a silikou, další vývoj kalibračního materiálu, který byl navržen patentem CZ 304580 B6, sledování nastavení Dispergraderu a porovnání staré a nové verze přístroje Dispergarder.

V této práci bylo zjištěno, které skleněné kuličky se jeví jako nejvhodnější pro přípravu kalibračního dílce. Dále bylo nutné nalézt vhodné barvivo a bylo dokázano, že nejvhodnějším barvivem, které neovlivňuje měření je červená temperová barva.

Dále bylo také prokázáno, že nastavení Dispergraderu, doba expozice a práh pro obrazové vyhodnocení, mají určitý vliv na měření, proto pro zvýšenou reprodukovatelnost a přesnost výsledků je důležité je vzít v úvahu při měření.

Posledním cílem práce bylo porovnání staré a nové verze Dispergraderu- Dispergarder$^+$ a Dispergrader α-view. Porovnání ukázalo, že pokud má Dispergarder α-view nastavenou dobu expozice na specifický čas, obě zařízení vykazují porovnatelné výsledky.

Klíčová slova: elastomery, plniva, saze, silika, makrodisperze, Dispergrader, referenční materiál, reprodukovatelnost, doba expozice, práh pro obrazové vyhodnocení

ABSTRACT

This master thesis focuses on macro-dispersion evaluation in filled elastomers. State-of-art part describes elastomers, reinforcing fillers, mixing process, dispersion and most important methods for macro-dispersion evaluation.

Experimental part deals with the macro-dispersion via Dispergrader device, optical microscope employed in reflection mode. The aims of the thesis are to investigate distribution of the measured values with carbon black and silica fillers, also further development of calibration object proposed in patent CZ 304580 B6, investigation of Dispergrader settings and comparison of old and new version of the device.

In this study was found which glass spheres are suitable for the calibration object preparation. The calibration object was pigmented as customer market desires pigmented calibration object and red tempera colour showed to be an appropriate pigment, because it does not significantly influence the measurement.

It was also proved that Dispergarder settings, exposure time and threshold for image analysis, have an influence on the measurement and need to be considered for increased reproducibility and accuracy of measurements.

The last aim of the thesis was a comparison of the old and new Disapergrader device. Evaluation showed that when the exposure time of Dispergarder α-view is set on specific values, both devices show comparable results.

Keywords: elastomers, fillers, carbon black, silica, macro-dispersion, Dispergrader, calibration object, reproducibility, exposure time, threshold for image evaluation

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Finally, I would like to express my gratefulness to my father and my sister for their endless support and for always being by my side, because without them I would be nothing.

I hereby declare that the print version of my Master's thesis and the electronic version of my thesis deposited in the IS/STAG system are identical.

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Bc. Kristýna Jedličková

CONTENTS

INTRODUCTION

Evaluation of macro-dispersion does have a significant role in a rubber industry, because macro-dispersion characterizes the incorporation of the filler into a rubber and gives information about effectiveness of mixing process. Therefore it is important characteristics for manufacturers and customers.

Macro-dispersion evaluation can be divided to two groups according to their measurement principle:

- Optical measurements
- Measurements of particular rubber property related to dispersion

The reproducibility of macro-dispersion evaluation is specific and it does not depend only on the measurement device, but it is also influenced by compound itself. It is known that low macro-dispersion values have broad distribution and high macro-dispersion values have narrow distribution and in this work was found that in carbon black (CB) or silica samples the lower the macro-dispersion value is, broader the distribution is. Therefore it is neither possible to create calibration object with CB nor silica compound. Also precision statement for macro-dispersion evaluation according to ASTM D7723 is missing, but the solution for the current state-of-art is the calibration object proposed in patent CZ304580 B6 by J. Kadlcak and R. Cermak from Tomas Bata University in Zlin, Department of Polymer Engineering [57].

General aims of the master thesis concentrate on further development of this calibration object, measurements related to calibration object and also investigation of the measurement device settings, i.e. threshold for image evaluation and exposure time. The output of this investigation is recommendation of suitable settings in compliance with the current state-of-art to obtain relevant and reproducible results. There is also included the first investigation of comparison of older and newer version of the measurement device called Dispergrader in one particular case to suggest and recommend a direction how these two devices can be compared.

I. STATE-OF-ART

1 ELASTOMERS

Elastomers are elastic polymers, i.e., elastic macromolecular substances [1]. Elastomers are amorphous materials that consist of large macromolecules, built of thousands of monomers. They can be cross-linked. The important characteristic of elastomers is glass transition temperature (T_g), because below this temperature elastomers are supercooled liquid that behave like rigid solid. But above T_g, cross-linked elastomers will have rubber-like properties. Elastomers in the uncured state have T_g well below room temperature [2, 3]. They have ability to undergo large elastic deformation and in comparison to other materials they have lower Young´s modulus and higher yield strain [3, 4].

Rubbers are vulcanized elastomers, which are characterized by their cross-links between the elastomer chains. Cross-links join the molecular chains together. Rubbers are classified to eight groups according to their chemical structure of macromolecular chain, see Table 1 [4].

Table 1- Rubber classification [5]

Group identification	Chemical structure of the macromolecular chain
M	saturated hydrocarbon chain
R	unsaturated hydrocarbon chain
N	chain contains nitrogen atoms
O	chain contains oxygen atoms
Q	chain contains siloxane bond (-Si-O-)
T	chain contains sulphur atoms
U	chain contains together nitrogen and oxygen atoms
Z	chain contains together nitrogen and phosphorus atoms

Rubber vulcanization with sulphur or another agent, i.e. peroxides, metal oxides, isocyanates, establishes chemical cross-links between the polymers and makes rubbers more durable. There are also other ingredients, i.e. fillers, which are added to make rubber stronger, tougher, harder, to make them age better, to colour them and generally to impart specific properties to meet specific application needs.

Rubbers are used widely, their applications ranging from household to industrial products. Tires and tubes are the largest consumers of rubber, but it can be also used for door and window profiles, hoses, belts, matting, flooring, dampeners for the automotive industry, etc. [19].

2 FILLERS

Fillers are one of the group of additives that are used in rubber industry. It is possible to tailor and modify fillers to any application. Fillers can practically modify material properties, influence the design, manufacture and use. The elastomer applications base has greatly expanded as the use of fillers has increased [7].

According to ASTM International the filler is a *„solid compounding material, usually in finely divided form, which may be added in relatively large proportions to a rubber for technical or economic reasons“*[8].

2.1 Filler classification and characterization

Fillers can be divided regarding their reinforcing effect as:

- non-reinforcing so called inert
- semi-reinforcing so called semi-active
- reinforcing so called active [9 ─11].

R. N. Rothon [12] in his book refers to reinforcing fillers as particulate materials that are able to increase the tensile strength, the tear strength and the abrasion resistance of natural rubber. To a semi-reinforcing fillers as a particulate materials that are able to increase the tensile strength and tear strength, but does not improve abrasion resistance and also to a non-reinforcing fillers as materials unable to provide any increase in these properties.

The important properties of the fillers according to their ability to reinforce rubber are structure and particle size.

The term structure refers to the developing of complex tri-dimensional shapes, called aggregates, so the structure characterizes the number of particles fused together to form an aggregate. There are two types of structure and they are also shown in Figure 1:

- low structure (a)
- high structure (b) [10, 13].

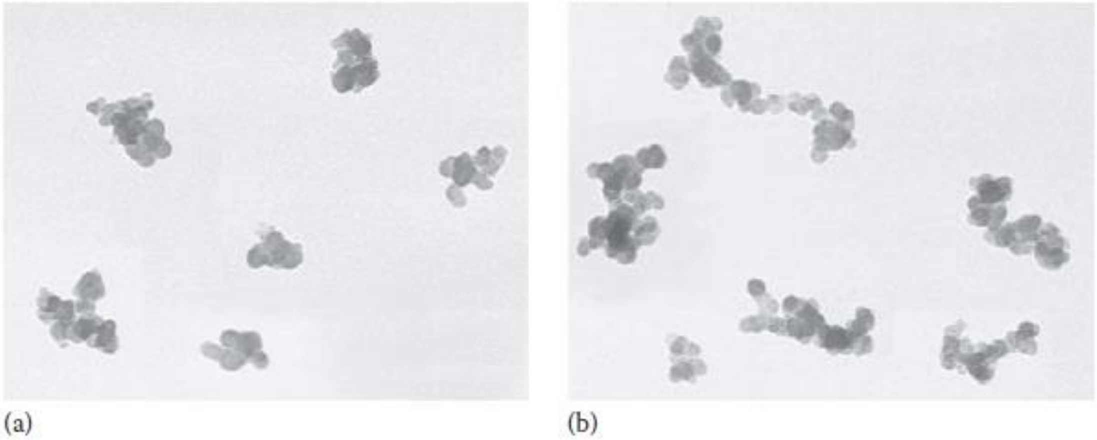


Figure 1- Low structured filler (a), high-structured filler (b) [13]

The structure of filler can be expressed quantitatively by the determination of liquid absorption or by the determination of specific volume at a given mechanical compression [14].

The particle sizes of fillers are complicated to determine because fillers are present as aggregates. Convenient method for particle size evaluation is an indirect measurement expressed by specific surface area (SSA), which is described as the surface area in square meters per unit mass of filler in grams available for an interaction with adsorbate. The nitrogen adsorption by powder fillers belongs to widely used method for the determination of surface and the activity or reinforcing capability of fillers. This SSA in m^2/g is calculated as follows:

$$S_w = \frac{N_\sigma . V_m}{M_v . W} \tag{1}$$

where N is Avogadro´s number, $6{,}023\times10^{23}$ molecules/g molecule, σ is the area occupied by one molecule of adsorbate - $16{,}2\times10^{-20}$ m^2 for nitrogen, V_m monolayer capacity in ml, M_v molar volume, and W is the sample weight in g [15─17].

The reinforcement effect is not the only reason, why fillers are added to a rubber. Some of the properties that can be also enhanced or changed by fillers are viscosity, optical properties and colour, thermal conductivity, heat dissipation, material resistance, stability, abrasion resistance, electrical conductivity, hardness, tensile strength, elongation, permeability, vibration damping, adhesion to substrates, etc. [12, 18].

3 REINFORCING FILLERS

This whole chapter is dedicated to reinforcing fillers, because this study is focused on them.

It is obvious that most usage of the rubbers would not be possible without adding the reinforcing fillers, because even vulcanized rubbers do not exhibit desired mechanical properties regarding its specific application [19].

Reinforcement increases the performance capability of a rubber and also improves the mechanical properties of rubber. This increase and improvement are accomplished by the incorporation of reinforcing fillers. The reinforcing capability is linked with the formation of a physically bonded flexible filler network and strong rubber-filler coupling, which are connected with a surface activity and the specific surface of filler particle [8, 20]. For example fillers with SSA less than 10 m^2/ g are classified as inert fillers and fillers with SSA higher than 60 m^2/g are reinforcing as well called active [10].

Reinforcement of rubbers by fillers is possible only in the rubbery state. In the glassy state, there is little or no reinforcement observed. The reason is that an infinite filler-rubber network, in case of carbon black called carbon gel, is a prerequisite for reinforcement. In the glassy state, below T_g, this network does not exist so the reinforcement observation is eliminated [16].

An important role in the rubber reinforcement is played by two effects- Mullins effect and Payne effect.

Mullins effect describes the softening of a vulcanized rubber. It is a result of a breakdown of the network structure, i.e. break-up of the association between filler and rubber chains. This effect occurs at large deformations, i.e. large strain amplitude, and it is irreversible [7, 8, 21].

Payne effect occurs at small deformation, i.e. small strain amplitude. It is related with the decrease in elastic modulus. When the amplitude of deformation is increased, disruption of the agglomeration network occurs and causes the decrease in modulus. This effect is reversible and it is observed in strain ranges between 0.1 % and 10 % [8, 14, 22, 23].

There are two reinforcing fillers in rubber industry, i.e. carbon black and silica, and they will be described later.

3.1 Carbon black

According to ASTM International carbon black (CB) is „*an engineered material, composed of elemental carbon, obtained from the partial combustion or thermal decomposition of hydrocarbons, existing as aggregates of acinoform, i.e. shaped like cluster of grapes, morphology, which are composed of spheroidal primary particles and turbostratic layering within the primary particles*“[24].

Table 2 gives an overview of elemental manufacturing processes of CB.

Table 2- Manufacturing processes of CB [10, 16]

Chemical process	Method	Raw material
thermo-oxidative decomposition	furnace black	aromatic oils from coal tart or petrol distillates, natural gas
	gas black- Degussa process	coal tart distillates, natural gas
	lamp black	aromatic oils from coal tart or petrol distillates
thermal decomposition	thermal black	natural gas or oils
	acetylene black	acetylene

Primary particles of CB are spherical with diameter dimension ranging from less than 20 nm to hundreds of nanometers. Primary particles are partially fused together to formulate larger units, called aggregates. They are the smallest dispersible unit of CB, because aggregates are very difficult, if not impossible to break during rubber mixing conditions due to their strong secondary bonding, i.e. Van der Waals forces. They can have diameter range to 300 nm. The only way how to separate primary particles from the aggregate is by fracturing. And a group of aggregates that are physically bounded with weak bonds and entangled together is referred as an agglomerate and they vary in size from less than a micrometer to a few millimeters as seen in Figure 2.

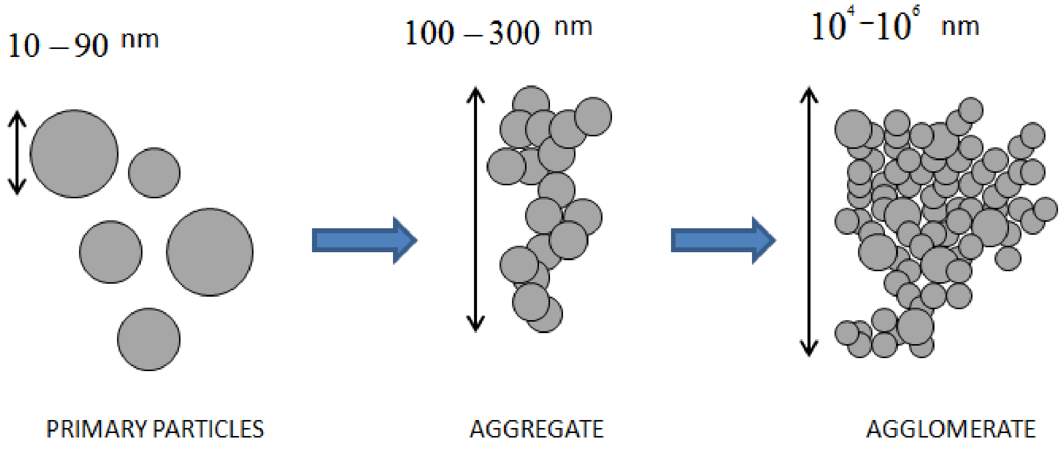


Figure 2- Primary particle- aggregate- agglomerate [56]

There can be made simple analogy between the clusters of grapes and the morphology of CB and this analogy is expressed with the word acinoform. In this analogy, the individual grapes are particles of CB and the cluster of grapes represents an aggregate.

CB aggregates play an essential role in rubber reinforcement, because the specific surface area and the structure of aggregates are important parameters in the ability of a given CB to reinforce a rubber. On the other side, the residual agglomerates are considered as failure initiation sites in filled compounds. Also the loading of CB has an influence on the imparted properties of filled rubber compounds [10, 15, 16, 18, 24, 25].

The classification of CB was firstly regarded to their manufacturing process and expected reinforcing character. Then the CB could be described with acronyms. i.e., high abrasion furnace as HAF [16]. Nowadays, ASTM International proposed standard classification and nomenclature described in ASTM D1765-14.

Four characters are used to describe rubber-grade CB, one letter and three numbers. The letter indicates the effect of the carbon black on the cure rate. That means that letter „N“ is used as description of normal curing rate and is related to furnace CB, that have not received any special modification. Letter „S“ is used for slow cure rate and get together channel or furnace CB that have been modified to reduce the curing rate of rubber. Digit that follows the letter corresponds to the average surface area of the CB as measured by nitrogen surface area. The nitrogen surface area range is divided to group and corresponding number is assigned to it as follows in Table 3:

Table 3- Groups related to nitrogen surface area [26]

Group no.	Average nitrogen surface area m^2/g
0	>150
1	121 to 150
2	100 to 120
3	70 to 99
4	50 to 69
5	40 to 49
6	33 to 39
7	21 to 32
8	11 to 20
9	0 to 10

The last two numbers are assigned arbitrarily [26].

In tire technology, it is possible to distribute CBs to the groups such as highly reinforcing, also called “tread” blacks with the average nitrogen area above 70 m^2/g. And semi-reinforcing, also called “carcass” blacks with the average nitrogen area between 21 to 69 m^2/g [10, 26].

Historically, CBs were used as pigments. Nowadays, their main purpose is the reinforcement of dynamic-mechanical properties, for example the incorporation of CB gives improved strength, extensibility, fatigue resistance, abrasion resistance, of performance rubber products such as tires [15, 27].

3.2 Silica

At present, synthetic silicas are used in rubber industries. The production of the synthetic silicas proceeds by precipitation as illustrated in Figure 3. The precipitation is formulated from a solution of alkaline silicates, so called water glass, through reaction with acids, including mineral acids such as sulphuric acid and hydrochloric acid, or metal salts. The final product is called precipitated silica.

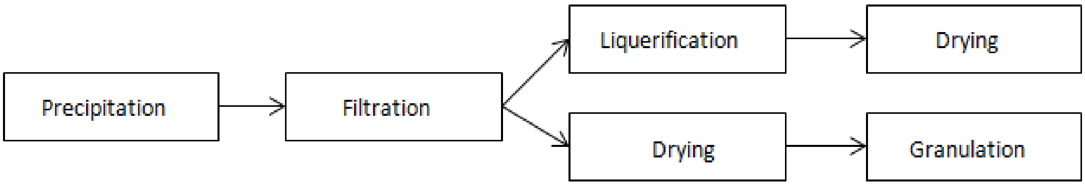


Figure 3- Precipitation manufacturing process [56]

Precipitation begins with formation of primary particles with size of few nanometers. During certain time, primary particles are bonding together with the Si-O-Si bonds and form aggregates of a few hundred nanometers. The number and size of aggregates is growing till the aggregate start to condense into larger units, agglomerates that are held together by van der Waals forces and hydrogen bonds.

The precipitated silicas can have specific surface area from 25 m^2/g up to 200 m^2/g, so it is classified as an active filler [18, 19, 22].

And the other process of silica production is the pyrogenation of silica tetrachloride, this process is carried out according to following reaction:

$$SiCl_4 + 2H_2 + O_2 \overrightarrow{\;1800°C\;} SiO_2 \downarrow + 4HCl \uparrow \qquad (2)$$

The final products are fumed silicas, which are used for silicone rubbers [10, 22].

The surface of silica consits of siloxane and silanol groups and as consequence its surface is strongly polar and hydrophilic. There is strong hydrogen bonding between silica aggregates and a stronger filler network thanks to silanol groups. This particular surface chemistry of silica can cause a special behaviour, such as silica surface can absorb significant quantities of water, moist silica is very difficult to dry or interparticle interactions are very strong because of hydrogen bonding as already mentioned above [19].

Also silica has weak filler-polymer interactions and strong filler-filler interactions. For improvement of mentioned weak filler-rubber bonding, silica modification, i.e. silanization, is necessary. Because of the filler-rubber bonding is increased, the reinforcement aspects are enhanced. Silanization can be achieved by addition of coupling agents that acts like a bridge between the silica and the rubber. Without coupling agent, the aggregates remain clustered in agglomerates, therefore bad dispersion and no reinforcement is obtained. Coupling agents are composed of silanes that have capability to react with silica surface and with the rubber. There are two tasks of coupling agent. Firstly, silica particle is hydrophobised by coupling agent and this leads to better dispersion and then secondly, it turns silica particle into a crosslink site that helps to chemically couple the rubber to the silica surface.

As one of the first proposed coupling agents was the 3-Mercaptopropyl(trimethoxy)silane MPTS, but this silane had a disadvantageous property. It produced unpleasant odour during mixing at high temperatures. Nowadays, the Bis(triethoxysilylpropyl)tetrasulfide TESPT is commonly used coupling agent.

The good dispersion of silica particles and an easy incorporation into rubber matrices determine positive effects on processing costs and on the performance of rubber products [22, 28, 29].

4 MIXING OF RUBBER

Rubber compounds are comprised from more than one component differing in properties, such as elastomers, fillers, oils and chemicals. Therefore, all components need to be incorporated into a rubber and also need to form a homogeneous blend. The mixing process provides this incorporation and homogenization and itself has an impact on a final compound, because bad mixing can result in less than optimum physical properties of final product.

There are some primary aims of mixing:

- to get a uniform mixture of all components in the mix
- to get an adequate dispersion of fillers
- to produce consecutive batches which are uniform in both dispersion degree and viscosity
- to minimize the labor, energy and equipment costs per unit volume of product [13, 14, 18].

The mixing process can be divided to four main components:

- incorporation- or so called wetting, is the first step of mixing, during incorporation the separated ingredients, i.e., rubber and additives, form a coherent mass and rubber is wetting and penetrating the filler and squeezing out trapped air
- dispersion- during dispersion filler agglomerates are fractured and reduced, literally broken down, to their ultimate size, i.e., aggregates which are the smallest dispersible unit, also the contact surface between the filler particles and the rubber is increasing and a good dispersion is achieved when force applied to the compound exceeds the cohesive force keeping the particles in agglomerate together
- distribution- means homogenization of the mix, during this process the filler positions are changed and randomly distributed throughout the mass of the mix to get a uniformity of the mixture, no particle breakdown occurs
- plasticization- addition of plasticizers finally modify the viscosity

These four stages of the mixing are not totally different and separated. They can take place throughout the whole mixing cycle [30 ─ 32].

Mixing of rubber is proceeded in a high-speed internal mixer. The main part of internal mixers is a temperature-controlled mixing chamber with a feed hopper and discharge door.

Other parts of the internal mixer are rotors which can exert both a high localized shear stress and a lower shear rate to the material being mixed, a ram which exerts pressure on the mix in the chamber and also heating/cooling systems, which control the temperature of the chamber walls, drop door, ram and rotors. The internal mixer can have two basic designs of rotors as illustrated in Figure 4:

- tangential type (a) - they can rotate independently and when necessary at different speeds, they also accept ingredients faster and discharge mixed compound faster so this is reason why they are useful in situations where high productivity is important, such as tire mixes
- intermeshing type (b) - they have to rotate at the same speed, they have a larger size of the chamber space and can take more material. Also they can give better dispersion degree, because they have more intensive mixing action. So they can perform better with mixes that are difficult to mix such as industrial goods [30]

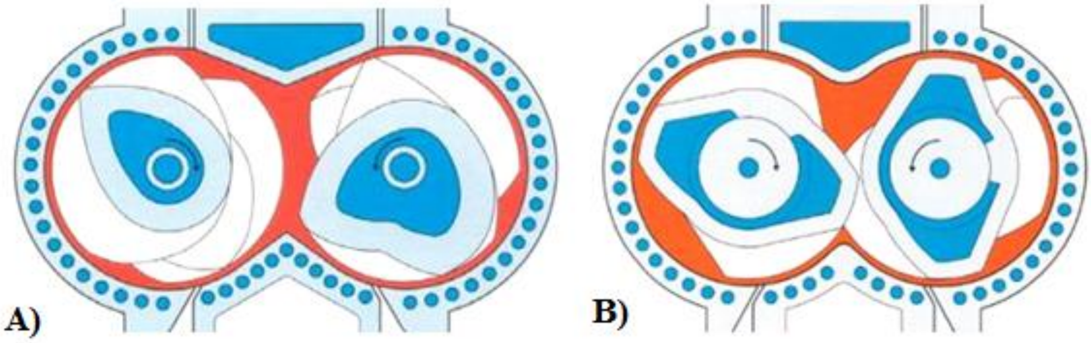


Figure 4- Tangential rotors (a), intermeshing rotors (b) [31]

The indicator of mixing is the degree of macro-dispersion in a rubber compound. It can give information about the effectiveness of mixing process [33].

5 DISPERSION

The term dispersion has several senses, but specially in this case it is used for a disperse system that is consisting of a solid filler dispersed in a rubber. It describes the degree of uniform distribution of a primary unit of filler, i.e. aggregates, into a compound. Dispersion is achieved by application of shearing forces. These shearing forces are distributing one or more compounding materials, such as fillers, uniformly throughout the mass of rubber [8, 24]. Filler dispersion is important and critical at the same time, because this factor affects the properties of filled rubber. The better filler dispersion can result in better mechanical and dynamical properties of final products. With poor dispersion some damaging aspects can occur, for example reduced product life or poor performance during service, poor product appearance, poor processing and manufacturing uniformity, waste of raw materials, excessive energy usage, etc.

At the beginning the filler itself is formed to agglomerates, then the filler needs to be incorporated into rubber by mixing and while mixing together, by applying a shearing forces higher than cohesive forces that holds aggregates together inside an agglomerate, occurs the dispersion. It is any process that breaks up an inhomogeneous, bad mixture and changes it into a smooth, homogeneous compound and after dispersion all particles of the filler are uniform and smaller in size in the whole volume of the rubber matrix. It is visually displayed in Figure 5. When there are any remaining undispersed agglomerates, they are considered as defects that generate material failure [6, 17, 19, 27, 39, 46].

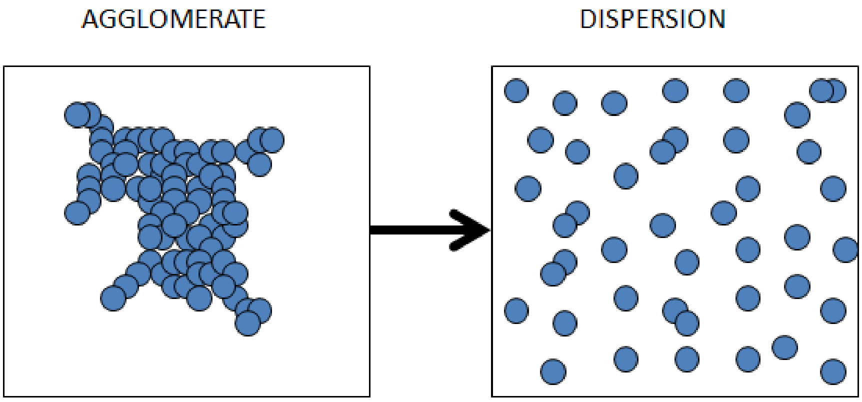


Figure 5- Agglomerate and dispersion [56]

There were identified two mechanisms of dispersion by Smits et. al. [34]. First one is the bulk rupture which is an abrupt breakage of the agglomerate into multiple large fragments. And the second one is the erosion which consists of a sequential removal of small fragments from the agglomerate periphery.

The residual, i.e. undispersed, agglomerates are not desired and refers to poor dispersion as it was mentioned earlier. For better imagination, the example of poor and good dispersion is shown in Figure 6.

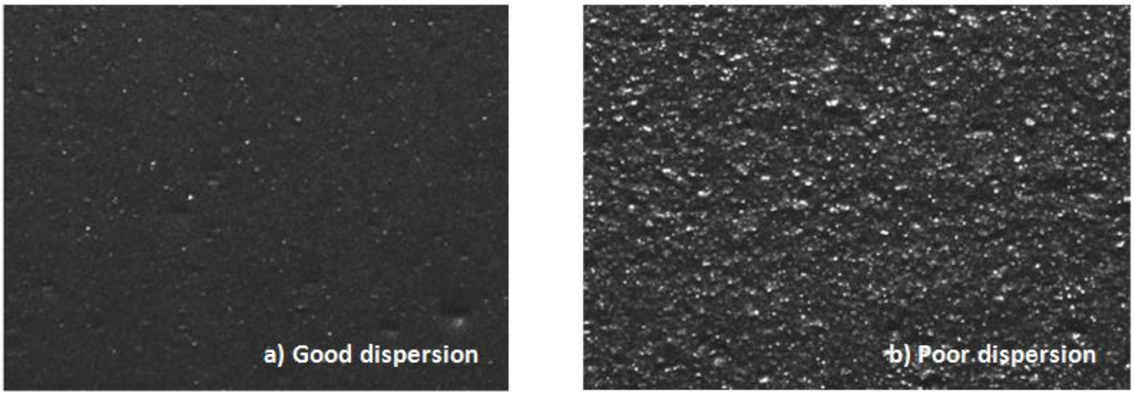


Figure 6- Good and poor dispersion of filler in rubber [56]

Filler dispersions are divided into two levels called micro-dispersion and macro-dispersion. Micro-dispersion characterizes the formation of the network and it is generally on scale of less than 2 µm. It can be evaluated for example with the scanning microscope or scanning probe microscope [24].

Macro-dispersion describes the incorporation of fillers into the matrix. It is a „*degree of distribution of filler into compound, generally on a scale of less than 100 µm but greater than 2 µm; represents micron range agglomeration*“[35]. Macro-dispersion is also an indicator of the mixing quality, it can give information about the mixing process effectiveness. It can be evaluated with light microscope, profilometer or interferometric microscope. The evaluation methods will be discussed in details in the following chapter, because this study deals with the macro-dispersion evaluation in filled elastomers, therefore it is necessary to introduce these methods in details.

6 METHODS FOR MACRO-DISPERSION ASSESMENT

As mentioned in chapter before the macro-dispersion is an indicator how good is the mixing process, i.e. its effectiveness. There are several methods for macro-dispersion evaluation. This chapter introduce some of them.

Vegvari and Hess [36] divided the methods for overall dispersion assessment into two categories:

- direct visual or optical analysis
- measurement of a particular rubber property, which is related to dispersion.

The following methods are proceeded according to three international standards: ISO 11345, ASTM D2663-14 and ASTM D7723-11 [35, 37, 38].

6.1 Direct visual or optical methods

6.1.1 Optical microscopy

It is an advantageous method, because it is an easy, versatile, user-friendly and cheap. It does not require any complicated sample preparation. The sample is any small piece of rubber and it does not require the knowledge of rubber type or CB loading. This sample is then directly evaluated by microscopist. Example of using optical microscope may be measurements according to ASTM D2663-14, method B. It is a method where agglomerates are counted manually. Microtome cuts with thickness less than 2 μm are required for this method. Agglomerates can be counted manually as was mentioned before or they are compared with reference classification table. Optical microscopy has also several disadvantages. For example it may be time consuming or at high magnifications the microscope objective is too close to the sample and there is some degree of subjectivity in measurements [17, 38 – 40].

Leigh- Dughmore introduced calculation of dispersion according to optical microscopy. Thin sections of rubber were measured in a light microscope, using transmitted light and total magnification of 100×. The dispersion is calculated as follows:

$$D = 100 - \frac{U_S}{L} \tag{3}$$

where U is total area of agglomerates, s is the areal swelling factor and L is total volume of CB [41].

Then few years later Medalia revised calculation of Dughmore calculation and came up with new equation regarding to the volume of filler present in agglomerates divided by the total volume of filler in order to get the fraction of filler which is undispersed:

$$D_n = 100 - \frac{vUs}{AL} \tag{4}$$

where U is the total number of squares covered by agglomerates, s is areal swelling factor, L is per cent by volume of carbon black in the whole unswollen stock, A is areal swelling factor for the agglomerates [42].

6.1.2 Image analysis

The sample is analysed directly in the microscope and the features in the image are analysed for different parameters at the same time, for example micrographs for size, shape and frequency of agglomerates. Agglomerates in the dispersion are counted on the basis of their longest scan line. Image analysis is applicable for online, automated full field feature specific imaging. D. Bieliński et. al. [43, 44] used image analysis for quality evaluation of CB and silica dispersions. Firstly, the surface morphology was examined with atomic force microscopy. Then taken images were evaluated through WSxM software from Nanotec Company.

Image analysis advantage lies in its ability to direct analysis of filler agglomerates for their percentage, size and spatial distribution. Disadvantage might be seen in difficult or time consuming specimen preparation and this method is suitable for low filler loadings [17, 39].

6.1.3 Dispergrader

It is applied for evaluation of the dispersion degree by comparing the roughness of the glossy sections or fracture surfaces with a number of reference samples. It becomes widespread and popular, because there is less involved preparation required and it gives reliable and reproducible results about the filler macro-dispersion.

This device proceeds measurements according to standards ASTM D7723-11 and ISO 11345- methods B, C, D and E. It can evaluate size and quantity of agglomerates and also it allows both, manual and semi-automatic measurements. Dispergrader α-view, also can be named as a new dispergrader, is portrayed in Figure 7.

Figure 7- Dispergrader α-view [45]

This device is an optical microscope that works in optical reflection mode. The light source sends a light beam onto a sample surface under 30 ° degree and this light beam then reflects from that surface. When the light beam strikes flat place on the surface, then it reflects away from optics. But when it strikes any agglomerate of filler it reflects into the optics, where this beam is transferred into computer form as figure. This principle is visually displayed in Figure 8. Grey scale image is obtained; agglomerates are displayed by white colour as white dots whereas flat places, i.e. rubber matrix, are displayed dark as shown in Figure 9. Then the software of Dispergrader changes the figure of sample surface into black and white duplicate, which is further used for figure analysis.

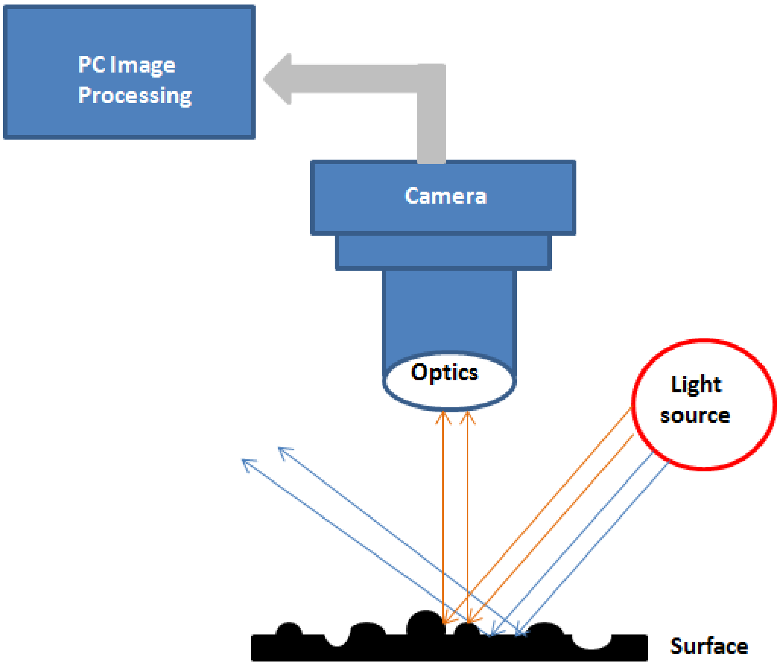


Figure 8- Dispergrader principle [56]

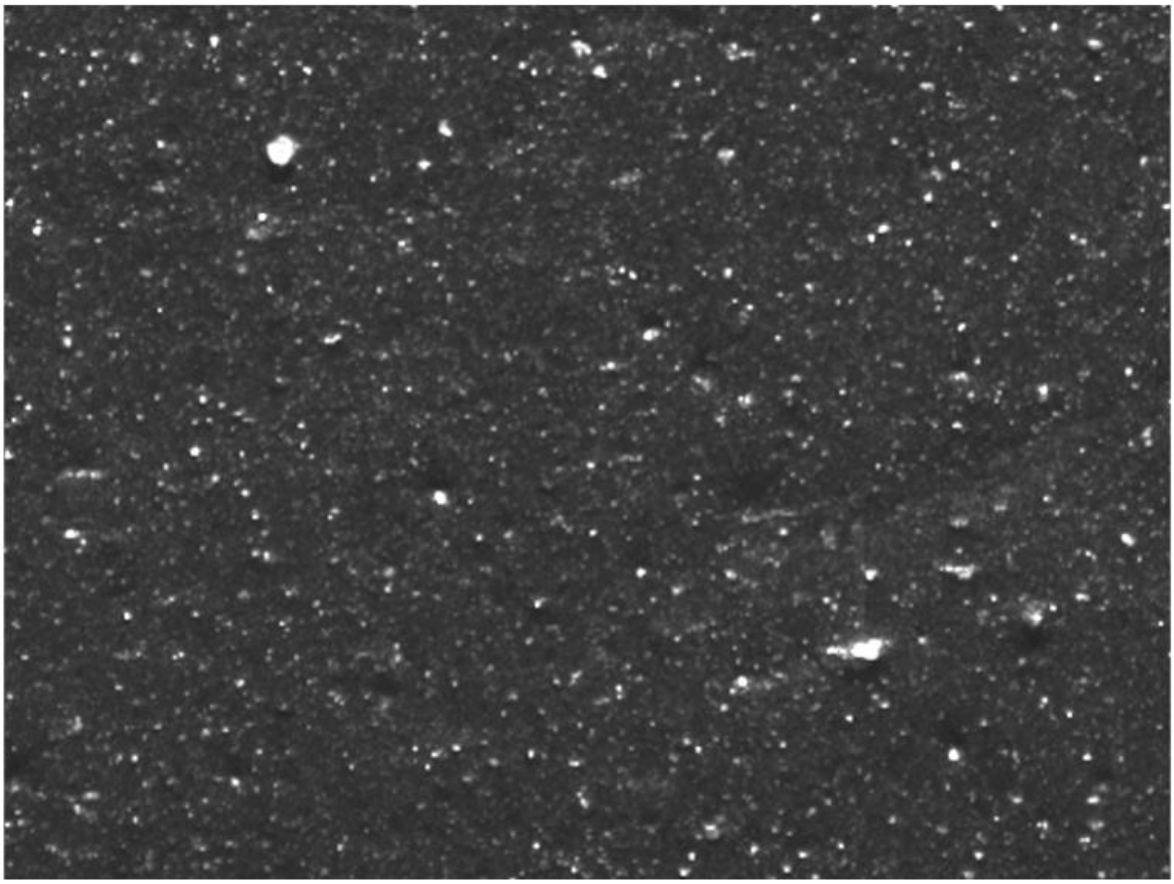


Figure 9- Example of obtained figure from Dispergrader device [56]

The test results are expressed on two numerical scales with range from 1 to 10 and two numerical value calculations:

- X value describes filler distribution.
- Y value is related to the occurrence of large agglomerates
- Dispersion value D % is a calculation based on the volume percentage of the filler that is input by the operator, and is defined in ASTM D7723.
- Z value was suggested by Otto et. al. [46] and it is based on the white area and constant 35, basically it measures how much less than 35 % the % white area is.

The final report from measurement also contains histogram of sizes and quantity of agglomerates.

There are several advantages of using dispergrader such as speed, directness and semi-automatization of the measurements [46 ─ 48].

6.1.4 Measurements according to ASTM D7723-11

The standard ASTM D7723-11 describes macro-dispersion characterization in a rubber matrix by quantifying the surface roughness of a freshly cut specimen using an optical microscope in reflection mode. This method can measure the dispersion quality of reinforcing fillers such as silica and CB, but also it is applicable as well as for inert fillers- chalk, clay and other solids. Other advantage is, that this measurement can be used also for coloured rubber. Only disadvantage is the missing precision statement.

According to the standard, the reflected light microscope used for measurements needs to have imaging power to resolve to 1 µm, 3µm or 10 µm and dark field illumination.

Percent dispersion can be calculated based on this area ratio as follows:

$$Dispersion\ \% = \frac{100-100.U_{RF}\%}{L} \tag{5}$$

where U_{RF} % is percentage of total scan from of undispersed filler measured in reflection and L is the filler volume fraction in the compound.

For verification and accuracy can be the filler volume fraction (L) calculated too:

$$L = \frac{compound\ density\ .\ filler\ mass}{filler\ density\ .\ compound\ mass} \tag{6}$$

When the L value is not given or unknown, the weighted percent dispersion or Z value is needed to be calculated by following expression:

$$Z\ value = \frac{100-100.U_{RF}\%}{0{,}35} \tag{7}$$

where U_{RF} % is percentage of total scan from of undispersed filler measured in reflection and number 0.35 is there, because Z value assumes a maximum of 35 % white area.

The test specimen for this measurement is prepared of a filled rubber compound. The thickness of a sample rubber compound should be between 5 and 10 mm, because thicker samples can influence the quality of the cut.

Overall procedure is simple. The specimen needs to be placed in front of the testing window right after cut. Five scans of different locations are recommended. And lastly calculations mentioned before are applied [35].

6.2 Measurement of particular rubber property related to the dispersion

6.2.1 Mechanical scanning microscopy (MSM)

The tool of this method is a surface profilometer with a 2 mm diamond tip stylus. This measurement is performed according to ASTM D2663- method C- stylus surface determination. The tip is moving over the surface of the freshly prepared rubber sample. Surface roughness measurements are an indirect measure of dispersion because the stylus does not directly measure the filler agglomerate. The surface texture is defined by several parameters such as profile, roughness and waviness.

The results of the MSM can be expressed as parameter R_a that is being given by:

$$R_a = \langle \bar{Z} - Z \rangle \tag{8}$$

Where Z the altitude of a point of the surface and $\bar{Z}$ is the average altitude of the surface. The smaller the R_a is, the better filler dispersion is. Typical MSM data are displayed in Figure 10.

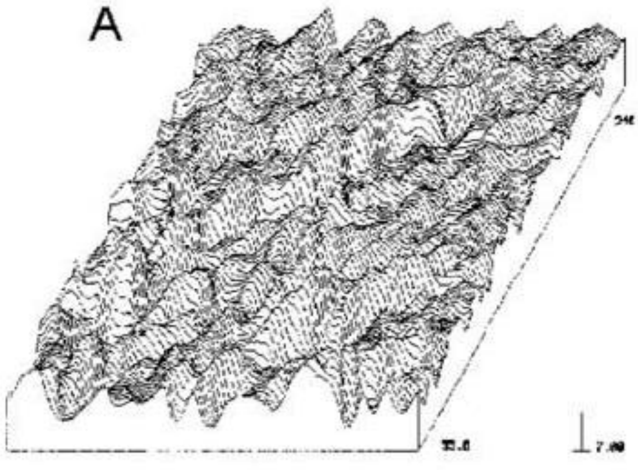


Figure 10- Typical MSM data [13]

The advantages of this method include the simple sample preparation and data manipulation. The disadvantages are that it can be applied only to cured compounds and if the tip pressure is not adjusted, it may cause damage to the surface [36, 39, 49].

6.2.2 Electrical measurements

Electrical measurements include the direct current measurements (DC) and the measurement involving alternating current (AC). The principle is based on fact that some fillers dispersed into rubber work as a conductive probe. As an example might be listed CB, because there is no current going through the sample, when CB agglomerates are dispersed into aggregates and these aggregates are separated from each other.

AC method, also impedance spectroscopy, is a perturbation-response measurement technique wherein the rubber sample is excited from an initial steady-state condition by a periodic electrical stimulus and the electrical response is then monitored. This measurement shows that there is a correlation between the resonance frequency and the dispersion level of conductive filler. As advantage can be considered fact that it is applicable to uncured compounds.

DC method is also applicable to cured as well as uncured compounds. Three types of measurement use DC technique:

- volume resistivity- simple volume resistivity can provide information not only on dispersion, but also about the kinetics of dispersion, polymer-filler interactions and can classify the polymers in order of CB dispersion and this method could be applied for cured and uncured samples
- current vs. voltage measurements- during the dispersion process the average distance among carbon black aggregates, δ, increases; as this method is sensitive to a parameter δ it allows to correlate these measurements with dispersion
- surface resistivity- essentially higher resistivity means better dispersion

The big disadvantage is that this method is not suitable for all fillers, for example silica cannot be evaluated with electrical measurements, because silica does not work as conductive probe [49 – 51].

7 STATISTICAL METHODS FOR RESULTS EVALUATION

Statistical methods are introduced, because experimental results are evaluated with the statistics for the accuracy. The testing of statistical hypotheses is a proper tool for the requirements of proceeded study.

Testing of statistical hypotheses procedure has several steps. Firstly, the formulation of the hypothesis is necessary, then is time to choose the α number which is probability of error-α is related to the risk that the hypothesis may be rejected although it is right. Related tested value needs to be calculated and compared with the related critical value from statistical tables. When the tested value is lower than critical one, zero hypothesis is accepted or when the tested value is higher than critical, zero hypothesis is rejected [52].

When two variances of groups using sample data are compared, then the F-test is used. The samples needs to be independent and the groups are distributed with N_1-1 and N_2-1 degrees of freedom, where N is sampling.

Zero hypothesis for the F-test is:

$$H_0: \sigma_1^2 > \sigma_2^2 \tag{9}$$

where σ_1^2 is variance of the first tested group and σ_2^2 is variance of the second tested group.

The formula for F-test is calculated as follows:

$$F = \frac{s_1^2}{s_2^2} \tag{10}$$

where s_1^2 is variance of the first tested group and s_2^2 is variance of the second tested group.

Calculated F value is then compared with critical F value from the tables or calculated in EXCEL with a tool FINV(α; N_1-1;N_2-1), where α is probability of an error, for example in science is probability of error 5 % and in quality it is 1 %, and N_1-1, N_2-1 are degrees of freedom of the tested groups. If the F value is lower than critical F value, the zero hypothesis can be accepted, but if the F value is higher than the critical F value, the zero hypothesis needs to be rejected [53 – 55].

When comparing influence of a factor, advanced substitute of an F-test called analysis of variance, ANOVA, is needed. As an example may be mentioned, comparison of machines, the different settings of the machine, etc. The simplest type of analysis of variance is the one-factor or one-way. The observed variance in a particular variable is partitioned into components related to different sources of variation as illustrated in Figure 11 and another assumption necessary for ANOVA is that the tested samples need to be independent.

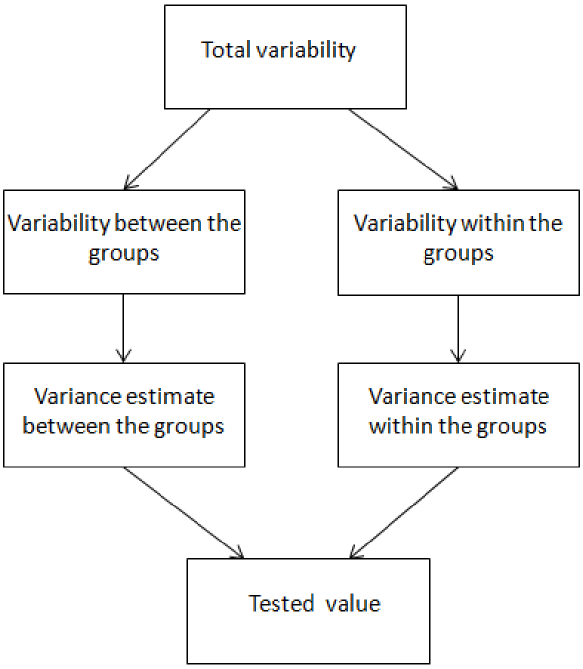


Figure 11- Sources of variation [56]

Zero hypothesis of one-factor ANOVA is:

$$H_0: \sigma_F^2 = 0 \tag{11}$$

where σ_F^2 is variance of factor and this hypothesis means that factor does not have an influence. When the zero hypothesis is true, the two estimates of variability, between the groups and within the groups, would reflect only random error. On the other side, when the zero hypothesis is false, both estimates would reflect random error, but also will reflect the factor effect, which means that factor has an influence.

The one-factor ANOVA can be summarized as Table 4.

Table 4- ANOVA table

Source of variation	Sum of squares SS	Degrees of freedom dF	Mean square MS (variance estimate)	F tested
Between the groups	SS_B	G-1	$MS_B = \frac{SS_B}{G-1}$	$\frac{MS_B}{MS_W}$
Within the groups	SS_W	N-G	$MS_W = \frac{SS_W}{N-G}$	
Total	SS_T	N-1	$\frac{SS_T}{N-1}$	

Where SS_B, SS_W necessary for the tested value can be calculated as follows:

$$SS_B = N.\sum_{k=1}^{G}(\bar{X}-\bar{X}_k)^2 \tag{12}$$

$$SS_W = \sum_{k=1}^{G}\sum_{j=1}^{N}\left(\bar{X}_k - X_{kj}\right)^2 \tag{13}$$

where N is the sampling in the group, $\bar{X}$ is the main mean value of the whole set of values, $\bar{X}_k$ is the mean group value and X_{kj} are all values in the group.

Calculated F value is then compared with critical F value from the tables or calculated in EXCEL with a tool FINV(α; N-G;G-1), where α is probability of an error and N-G, G-1 are degrees of freedom. When the F value is lower than critical F value, the zero hypothesis can be accepted, but when the F value is higher than the critical F value, the zero hypothesis needs to be rejected [53, 55]. When the zero hypothesis is rejected, it is clear that there are groups differing from each other. It is possible to check which ones exactly with the simple Scheffé´s method [52] of comparison:

$$|\bar{X}_n - \bar{X}_k| \geq \sqrt{\frac{G-1}{N-G}.SS_W.F_{critical}.\left[\frac{1}{N_n}+\frac{1}{N_k}\right]} \tag{14}$$

where $\bar{X}$ represents mean values, G number of groups, N sampling and SS_W sum of squares within the group [52].

II. EXPERIMENTAL PART

8 AIMS OF THE MASTER THESIS

On the basis of assigned tasks and literature survey, the main aims of the master thesis are described as follows:

- Investigate the influence of the dispersion degree on distribution of the measured values.
- Further development of the calibration object for macro-dispersion evaluation proposed in patent CZ304580 B6 [57] in compliance with ASTM D7723 [35], including: sample preparation, description of used materials, microscopy of the glass spheres, image analysis for size distribution of the glass spheres and investigation for finding a suitable pigment for calibration object and measurements related to calibration object.
- Investigate the measurement device settings, i.e. Dispergrader α-view. The setting is including exposure time and threshold for image analysis or described also as dispersion threshold.
- Comparison of Dispergarder$^+$ with the Dispergrader α-view.
- Discussion of the results.

9 DISTRIBUTION OF THE MEASURED VALUES

Evaluation of distribution of measured values was proceeded to explore whether the degree of the dispersion, also referred as dispersion value, has any significant influence on the distribution of the measured values. Have the overall range from high dispersion degree to low dispersion degree the same distribution of the measured values? Or is there any difference among the range of dispersion degree?

For distribution of the measured values were chosen two groups of samples with added reinforcing filler. First group are twenty-five samples with CB filler and the second group are twenty-five samples with silica/CB filler. All samples were provided by Continental Reifen Deutschland GmBH, Hannover. In this case composition of the mixture is not an important information, because this is evaluation of influence of the factor, i.e. influence of dispersion degree.

Each sample was measured ten times, so the total number of the group measurement was 250 measurements to evaluate wide range of the dispersion values. And the dispersion degree of the samples were measured with the Dispergrader$^+$ (OD). Measurements were performed at a room temperature, approximately 25 °C. The sample was cut with sharp razor blade to obtain freshly exposed surface, the thickness of the cut is recommended to be between 5 to 10 mm. Each cut was placed in front of the testing window and scanned five times at different locations with the OD. And then software of the device applies calculations and mean dispersion value of these five scans is obtained. Further information about Dispergarder measurement technique are included in Chapter 6. CB samples were divided to four equidistant groups according to their dispersion degree results as follows in Table 5:

Table 5- Groups of CB samples

Group	Dispersion degree (D %)
1	96 ─ 100 %
2	85 ─ 95 %
3	70 ─ 84 %
4	69 % and lower

Results of the measurements are displayed in Table 6, which shows average values, standard deviations and errors of each group.

Table 6- Averages, standard deviations and errors of CB groups

D %	96 ─ 100 %	85 ─ 95 %	70 ─ 84 %	69 % and lower
Average	98.7	92.2	78.1	58.5
Standard deviation	0.8	3.0	5.1	6.7
Error	0.1	0.7	2.6	2.0

It is obvious that values are different and highest errors are observed in the groups with D = 70 ─ 84 % and 69 % and lower.

Then measured values were evaluated with the ANOVA tool, because in this case the evaluation investigates an influence of the factor.

Zero hypothesis: Level of dispersion degree does not have influence on the distribution of the measured values.

$$H_0\colon \sigma_F^2 = 0 \tag{15}$$

Alternative hypothesis H_1 is described as:

$$H_1\colon \sigma_F^2 > 0 \tag{16}$$

Table 7 summarizes sampling, groups, degrees of freedom among and within the groups and the probability of error.

Table 7- Sampling, groups, degrees of freedom of CB groups

Sampling - N	250
Groups - G	4
Degrees of freedom among the groups- G − 1	3
Degrees of freedom within the groups- N − G	246
Probability of error - α	0.05

Results of ANOVA are displayed in Table 8.

Table 8- ANOVA results of CB samples

	Sum of the square deviations	Degrees of freedom	Mean square (variance estimate)
Variability between the groups	66049	G-1= 3	22016
Variability within the groups	3110	N-G= 246	13

Tested value and critical value for ANOVA are calculated as follows:

$$F_{tested} = \frac{22016}{13} = 1693{,}5 \doteq 1694 \tag{17}$$

$$f_{critical} = f_{(0.05;3;246)} = 3 \tag{18}$$

$$1694 > 3 \quad \rightarrow F_{tested} > f_{critical} \tag{19}$$

Zero hypothesis is rejected. The level of dispersion degree has an influence on the distribution of the measured values.

For investigation whether there are groups with same distribution was used Scheffé´s method [52] of comparison included in Table 9.

Table 9- Scheffé´s method of comparison of the CB samples

Compared groups	$\lvert\bar{X}_n - \bar{X}_k\rvert$	$\sqrt{\frac{G-1}{N-G}.SS_W.F_{critical}.\left[\frac{1}{N_n}+\frac{1}{N_k}\right]}$
96 — 100% and 85 — 95%	6.5	1.5
96 — 100% and 70 — 84%	20.6	2.6
96 — 100% and 69% and lower	40.2	1.7
85 — 95% and 70 — 84%	14.1	2.7
85 — 95% and 69% and lower	33.7	1.9
70 — 84% and 69% and lower	19.6	2.8

As seen in the Table 9, it is obvious that lower the dispersion degree is, seen in column with compared groups, the broader the distribution of the measured values is.

Silica/CB were evaluated with the same method as CB samples. They were also divided to equidistant groups according to their dispersion degree results, but this time there are five groups as seen in Table 10. Measurement results are shown in Table 11, where is possible to see average values, standard deviations and errors.

Table 10- Groups of silica/CB samples

Group	D %
1	90 – 100 %
2	94 – 97 %
3	85 – 93 %
4	75 – 84 %
5	74 % and lower

Table 11- Average values, standard deviations and error of silica/CB samples

D %	98 – 100 %	94 – 97 %	85 – 93 %	75 – 84 %	74 % and lower
Average	98.9	96.5	89.1	80.2	71.4
Standard deviation	0.4	1.0	1.6	2.9	2.6
Error	0.1	0.2	0.5	1.4	0.8

Zero hypothesis and alternative hypothesis are the same as the zero hypothesis and alternative hypothesis of CB samples.

Table 12 summarizes sampling, groups, degrees of freedom among and within the groups and the probability of error.

Table 12- Sampling, groups, degrees of freedom of silica/carbon black groups

Sampling - N	250
Groups - G	5
Degrees of freedom among the groups- G ─ 1	4
Degrees of freedom within the groups- N ─ G	245
Probability of error - α	0.05

Results of ANOVA are displayed in Table 13.

Table 13- ANOVA of the silica/CB samples

	Sum of the square deviations	Degrees of freedom	Mean square (variance estimate)
Variability between the groups	27344	G-1= 4	6836
Variability within the groups	576	N-G= 245	2.4
Tested value	2848		
Critical value	2.4		

Zero hypothesis is rejected. The level of dispersion degree has an influence on the distribution of the measured values.

Scheffé´s method for comparison [52] was also used and the results are the same as in the case of CB samples.

Table 14- Scheffé´s method of comparison of the silica/CB samples

Compared groups	$\lvert \bar{X}_n - \bar{X}_k \rvert$	$\sqrt{\frac{G-1}{N-G}.SS_W.F_{critical}.\left[\frac{1}{N_n}+\frac{1}{N_k}\right]}$
98 − 100% and 94 − 97%	2.4	0.8
98 − 100% and 85 − 93%	9.8	0.9
98 − 100% and 75 − 84%	18.7	1.2
98 − 100% and 74% and lower	27.5	0.9
94 − 97% and 85 − 93%	7.4	0.9
94 − 97% and 75 − 84%	16.3	1.3
94 − 97% and 74% and lower	25.1	1.0
85 − 93% and 75 − 84%	9.0	1.3
85 − 93% and 74% and lower	17.7	1.1
75 − 84% and 74% and lower	8.8	1.4

The same pattern is observed in the Table 14 and it is again obvious that the lower the dispersion degree, the broader the distribution of the measured values is.

10 FURTHER DEVELOPMENT OF THE REFERENCE OBJECT FOR THE MACRO-DISPERSION EVALUATION, I.E. CALIBRATION OBJECT

Calibration object proposed in Patent CZ304580 B6 [57] is a simple tool useful for calibration of the devices that measure quality of the filler macro-dispersion in rubber matrix. These devices utilize optical microscopy for quantification of the surface roughness on freshly cut specimen.

Calibration object could improve the quality of macro-dispersion evaluation, especially its reproducibility, because in previous chapter was found that with real CB or silica compound the lower the dispersion degree, broader the distribution of the measured values is. It is proposed consistently with ASTM standard D7723-11 [35]. This standard is still missing the precision statement, so the calibration object is a solution.

Three steps are necessary for the preparation process. First step concentrates on optical characterization of glass spheres via optical microscopy and subsequently image analysis evaluating size distribution of the filler. In the second step, silicone rubber is mixed with glass spheres and curing agent under specific conditions. Lastly, acquired mixture is poured into a mold, it is vacuumed and cross-linked.

10.1 Used materials

Reference object matrix is a silicone rubber (SR). It was chosen because it is supplied in a liquid form, therefore it is easy to mix it with fillers, it is easy to crosslink and its processability is good. Its availability on the market is also good. Because of all these reasons, SR is a proper matrix for calibration object. For calibration object is exactly used the Sylgard 184 from Dow Corning Company. Some of the typical properties of Sylgard 184 can be found in the Table 15.

Table 15- Typical properties of Sylgard 184

Property	Value	Unit
Viscosity	5.2	Pa.s
Tensile strength	7.1	MPa
Elongation	120	%
Durometer Shore A	44	-
Dielectric strength	19	kV/mm
Volume resistivity	2.9×10^{14}	ohm.cm
Dielectric constant at 100 Hz	2.72	-
Shelf life at 25 °C	48	months

And glass spheres (GS) were chosen as a filler. They were chosen because they are spherical, their degree of roundness is higher than 85%, they have narrow size distribution and they can simulate CB agglomerates. GS were supplied from companies Cospheric (COS) and Polysciences (PS). Typical properties of GS are displayed in the Table 16.

Table 16- Typical properties of COS and PS spheres

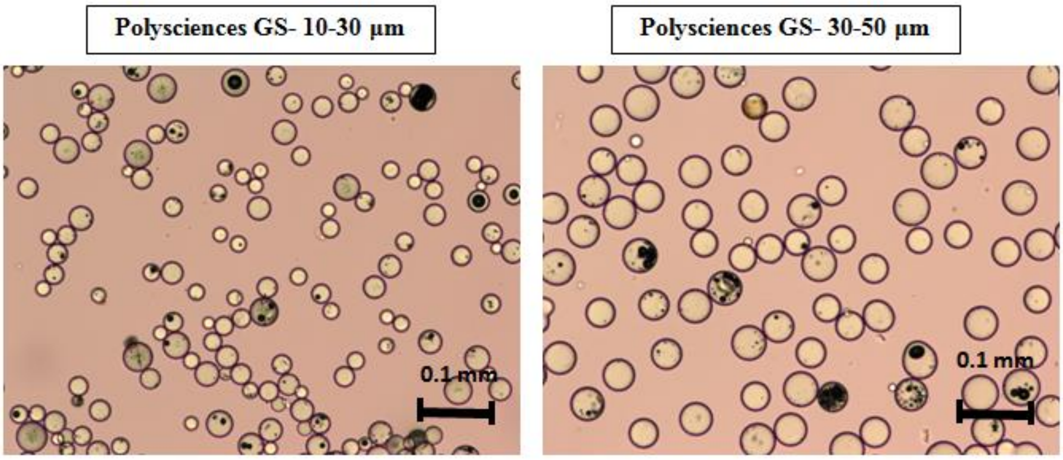
	COS spheres	PS spheres
Glass type	Type A soda-lime glass	Soda-lime glass
Size of the spheres	3 µm ─ 70 µm	10 µm ─100 µm
Refractive index	1.5	1.5
Degree of roundness	> 85%	─
Density	2.6 g.cm^{-3}	─

Table 16 continues here.

	COS spheres	PS spheres
Hardness	─	6.0
Volume resistivity	─	6.5×10^{12} ohm.cm

10.2 Microscopy of the GS and image analysis of the size distribution of the GS

Microscopic analysis were proceeded with a binocular optical microscope Olympus BH2 (JPN) under 100× magnification ─ 10× magnification of eyepiece and 10× magnification of lens. Each type of spheres was mixed with a drop of paraffinic oil on laboratory glass and then investigated in the optical microscope. 50 images of each type of glass spheres were taken. Figures 12 to 16 shows examples of taken images. The smallest spheres COS 3 ─ 5 µm were also analysed with higher magnification, 200× and 400× as displayed in Figure 16. Taken figures were used for image analysis. Image analysis evaluated the size distribution of the GS through the image processing software. Images 17- 23 demonstrates the histograms of size distributions.



Polysciences GS- 10-30 µm

Polysciences GS- 30-50 µm

Figure 12- Optical microscopy of PS GS, 10 ─ 30µm, 30 ─ 50 µm

Figures 12 and 13 demonstrates the GS of PS Company. As can be seen from the figures, the GS from the smallest fraction of 10 ─ 30 µm are branched together as they are forming agglomerates. With the fractions of 30 ─ 50 µm and 50 ─100 µm the branching is not that obviously observed as in the first case. From the macroscopic aspect the shape of the GS is evaluated as spherical.

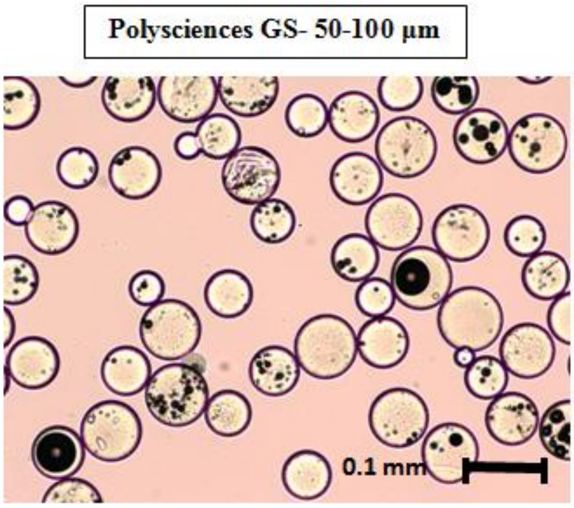
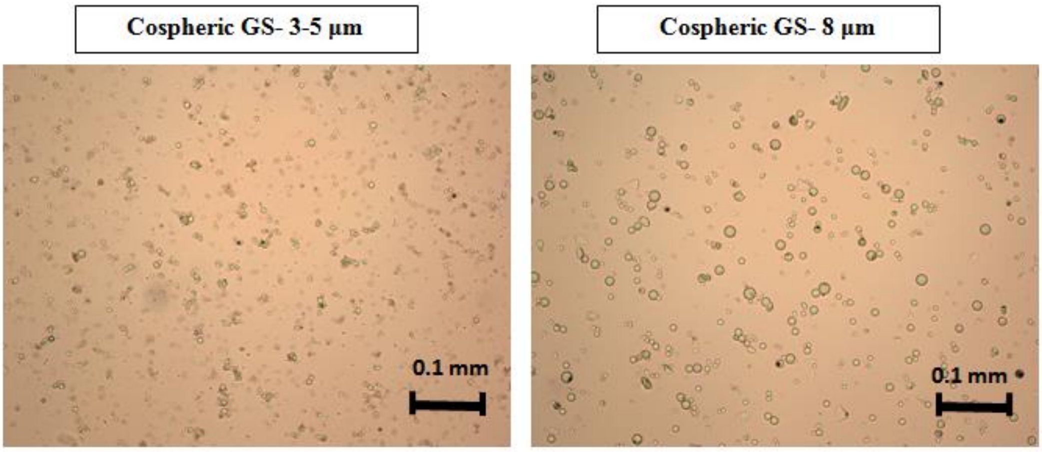

Polysciences GS- 50-100 µm

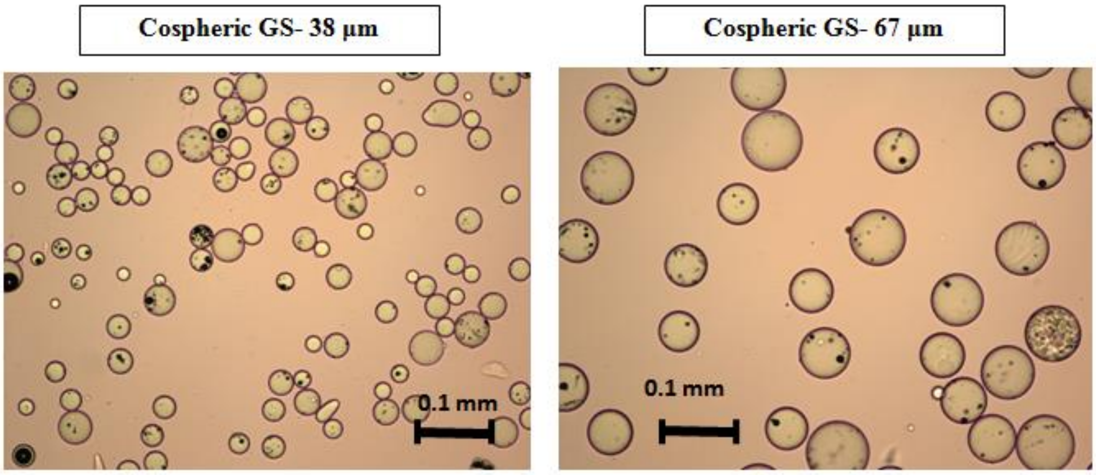
Figure 13- Optical microscopy of PS GS 50 ─ 100 µm


Cospheric GS- 3-5 µm

Cospheric GS- 8 µm

Figure 14- Optical microscopy of COS GS, 3 ─ 5 µm, 8 µm

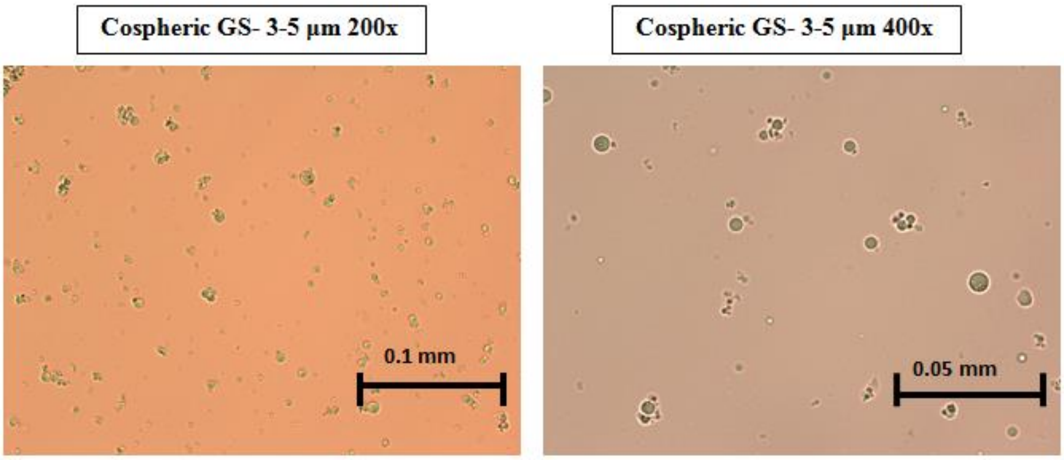
Figures 14 and 16 demonstartes the COS GS. Their shape is also evaluated as spherical from the macroscopic aspect and they are more branched than the PS GS. For the smallest fractions of 3-5 µm and 8 µm was necessary to increase magnification to 200× and 400× as the magnification of 100× is not sufficient for the size distribution analysis. The examples of figures of higher magnification are displayed in Figure 16. Magnifications 200× and 400× appear more suitable for image analysis, because at higher magnification it is possible to distinguish shapes and branching.



Cospheric GS- 38 µm

Cospheric GS- 67 µm

Figure 15- Optical microscopy of COS GS, 38 µm, 67 µm



Cospheric GS- 3-5 µm 200x

Cospheric GS- 3-5 µm 400x

Figure 16- COS GS 3 ─5 µm under 200× and 400× magnification

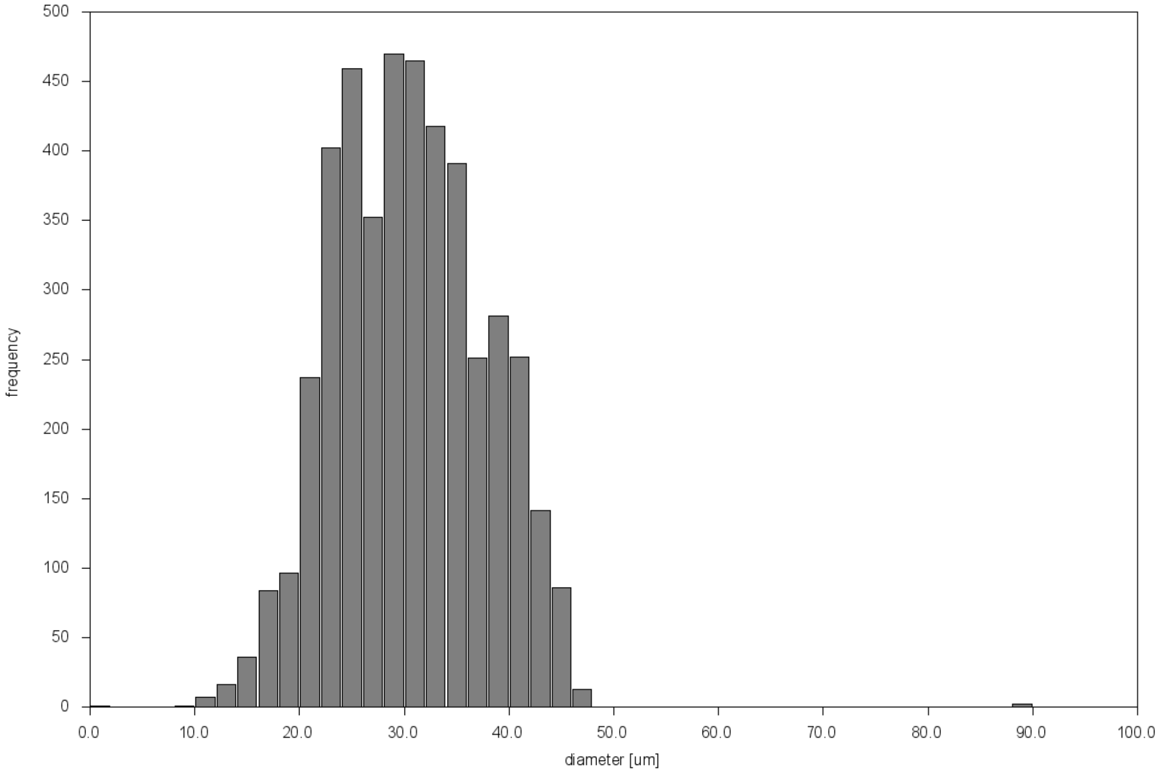


Figure 17- Histogram of size distribution, PS 10 ─ 30 um

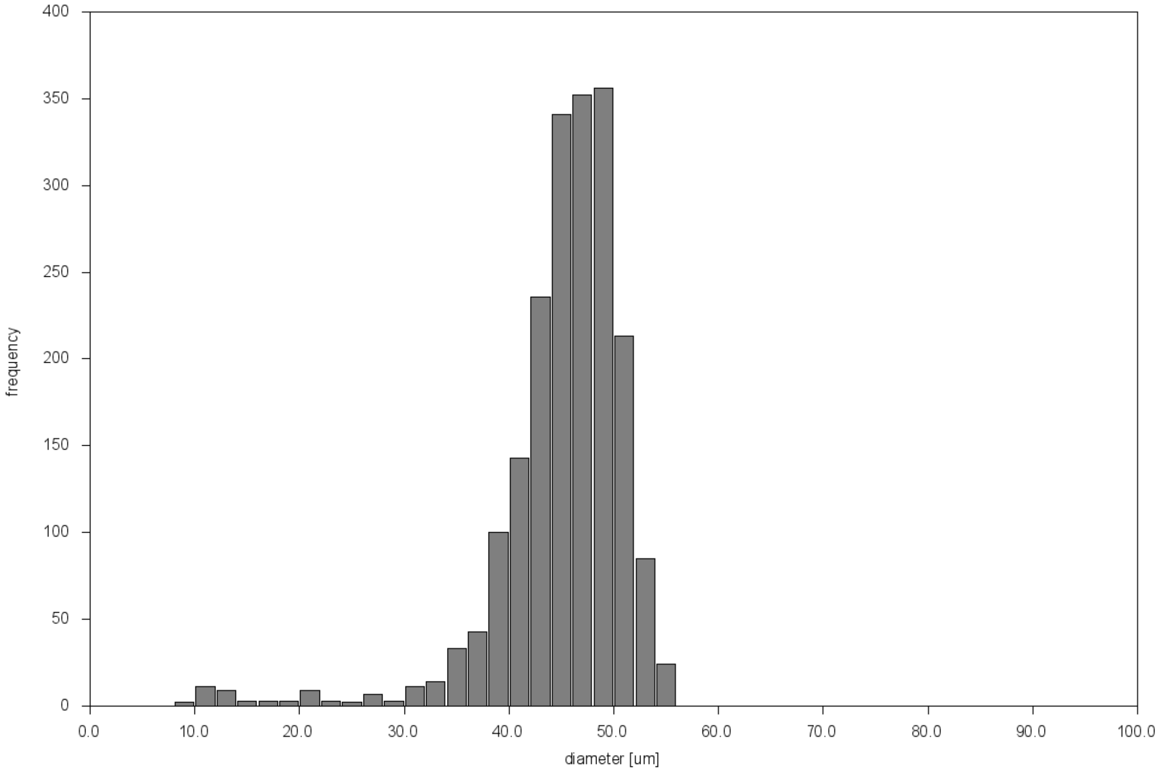


Figure 18- Histogram of size distribution, PS 30 ─ 50 um

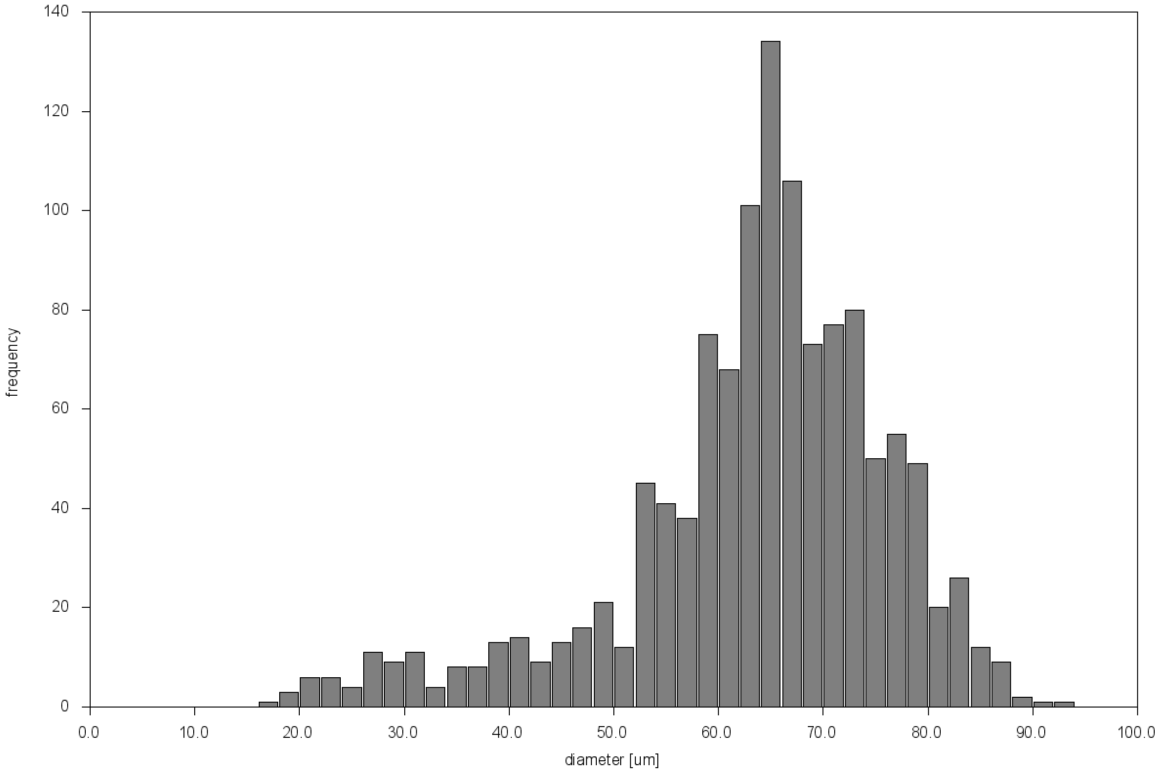


Figure 19- Histogram of size distribution, PS 50 ─ 100 um

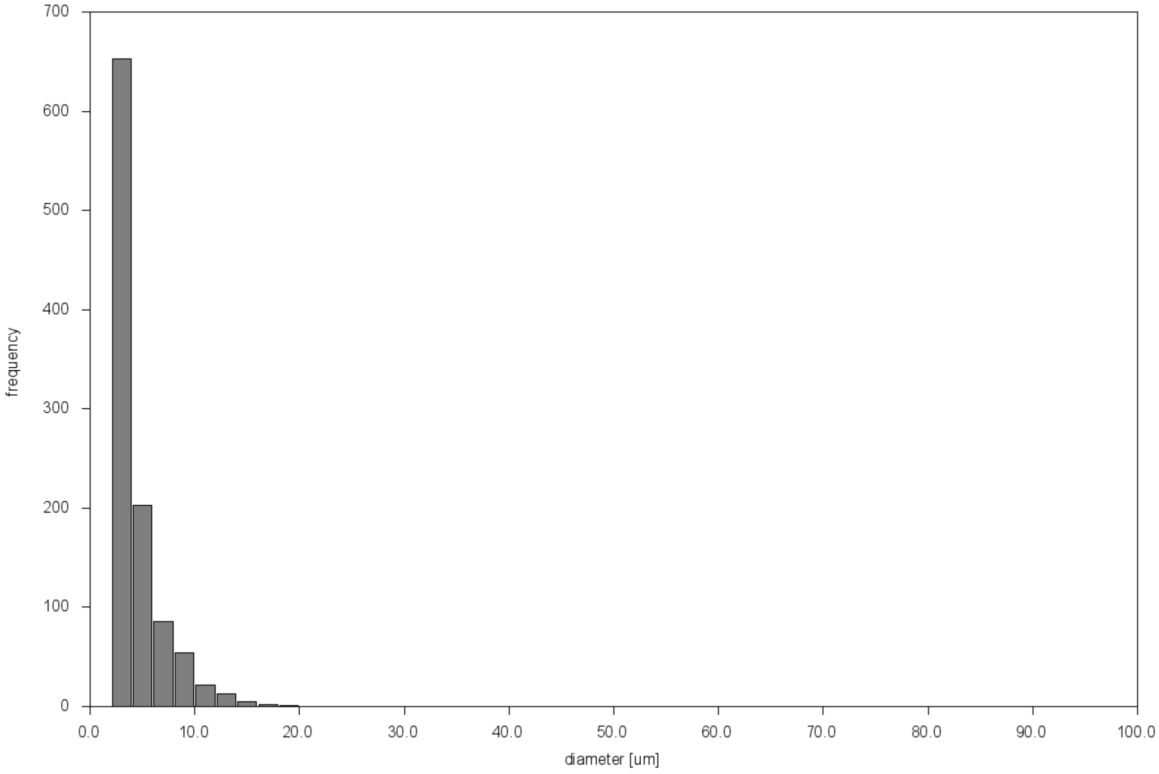


Figure 20- Histogram of size distribution, COS 3 ─ 5 um

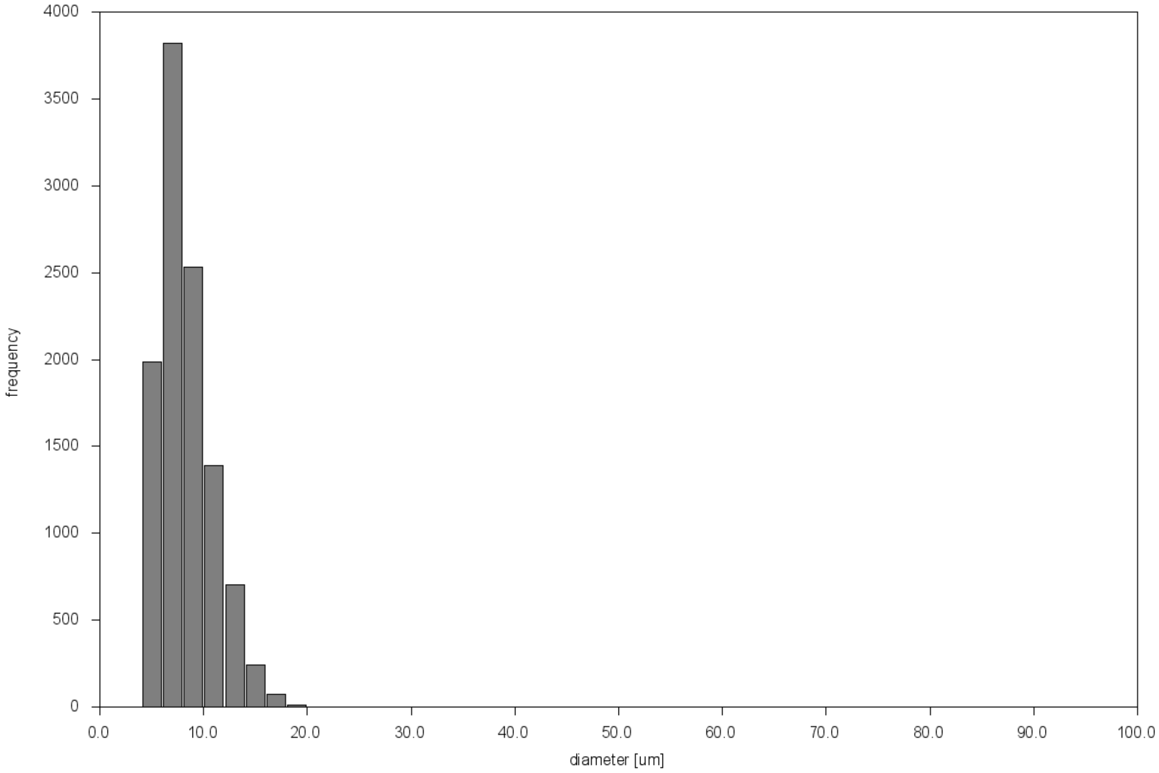


Figure 21- Histogram of size distribution, COS 8 um

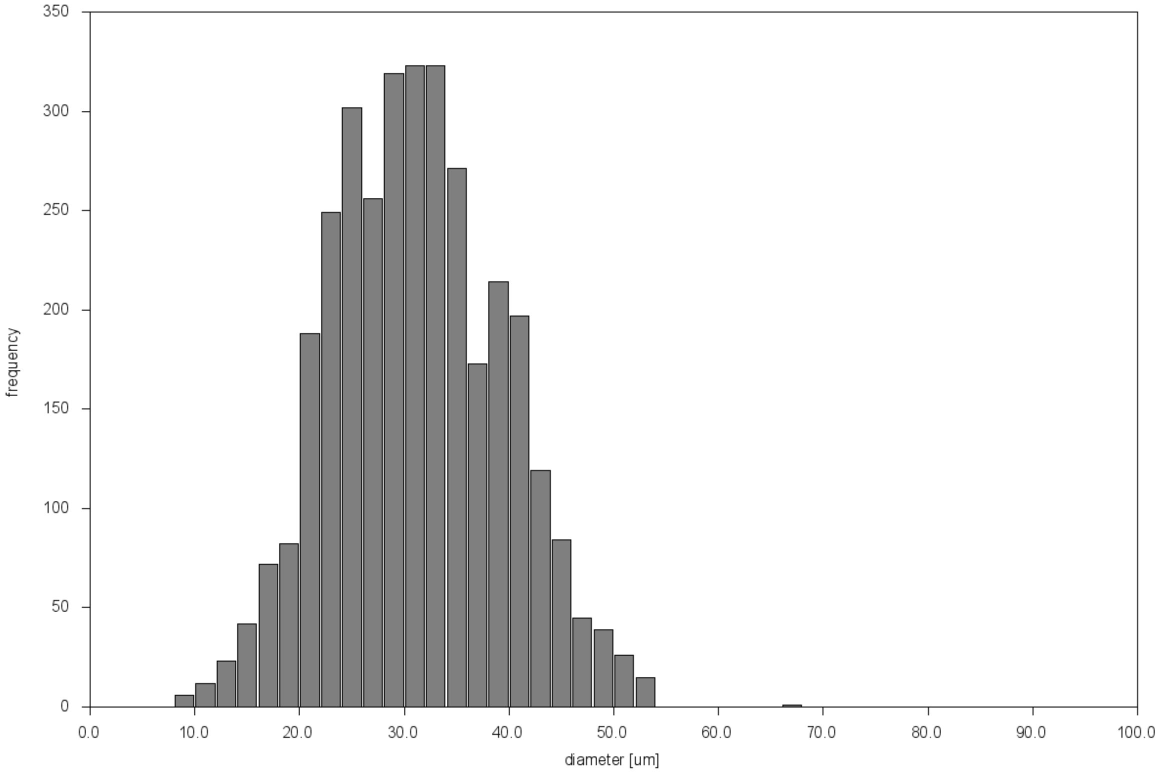


Figure 22- Histogram of size distribution, COS 38 um

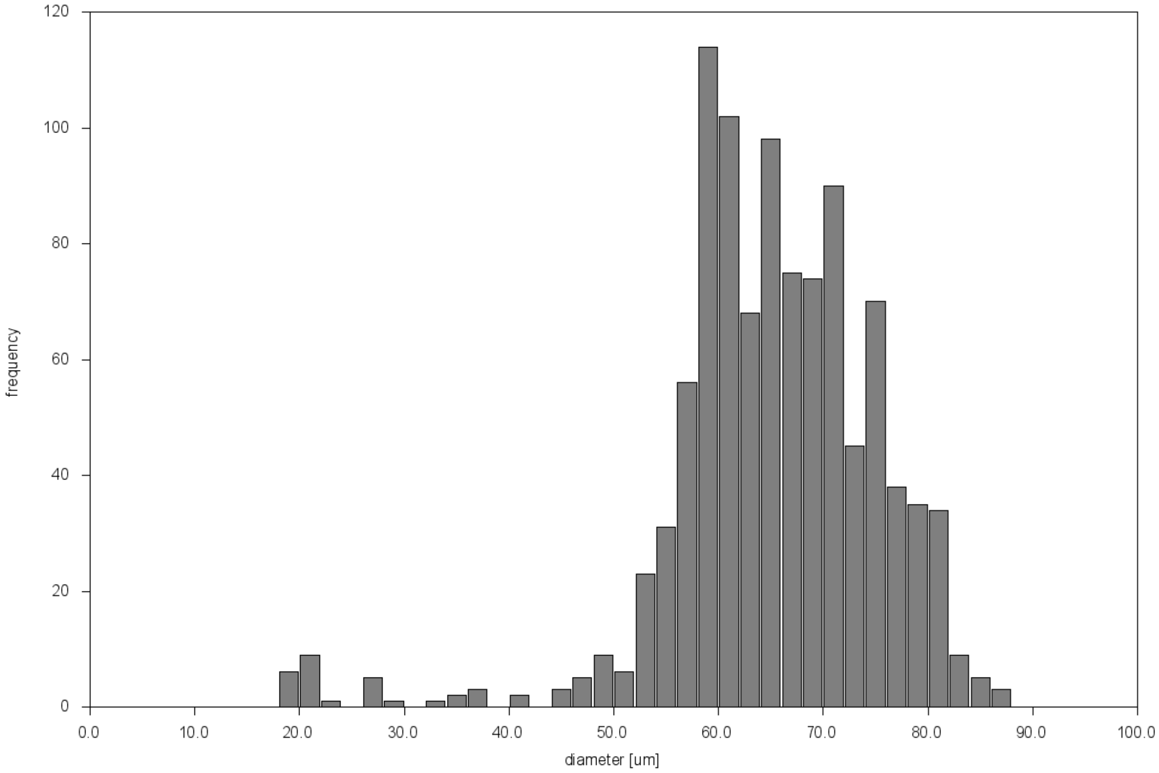


Figure 23- Histogram of size distribution, COS 67 um

From the histograms it is obvious that size distribution of the GS differs slightly from a manufacturer information and description. The broadest size distribution have PS GS with size 50 ─ 100 µm as seen in Figure 19 and these GS ranges from 15 µm to 100 µm so they are not suitable for further employment in calibration object. In the Table 17 are summarized median values and average values of each spheres size distribution according to image analysis.

Table 17- Median values and average values of each spheres size distribution

Type of GS	10 ─ 30 µm PS	30 ─ 50 µm PS	50 ─ 100 µm PS	3 µm COS	8 µm COS	38 µm COS	67 µm COS
Median	30.1 µm	46.3 µm	65.2 µm	3.4 µm	7.9 µm	30.9 µm	65.2 µm
Average	30.5 µm	45.1 µm	63.5 µm	4.3 µm	8.3 µm	31.2 µm	65 µm
Standard deviation	7.1	6.3	12.9	2.4	2.53	8.1	10.3
Error	0.2	0.2	0.7	0.1	0.05	0.3	0.6

For further investigation with calibration object were chosen the GS from COS Company with sizes 3 µm to 67 µ due to their narrow size distribution once demonstrated in histograms and also small errors and standard deviations show narrow distribution. Therefore their suitability for CB simulation is good.

10.3 Incorporation of GS into SR

This investigation was proceeded to find out which Z % values (Chapter 6.1.1) are possible to be obtained with GS with different sizes incorporated into SR. Chosen GS of sizes 3, 8 µm, 38 µm and 67 µm were stirred into SR and sample was cross-linked. The dosing of GS into SR in parts per hundred rubber (phr) is following 0.1, 1, 10, 25, 50 and 100 phr. Measurement were performed with old dispergrader (OD) Results are listed in Table 18.

Table 18- Z % values of different types of GS and different phr

3 µm- Z %	0.1 phr	1 phr	10 phr	25 phr	50 phr	100 phr
Average	97.2	98.1	99.3	99.79	99.95	99.998
Standard deviation	0.8	0.5	0.3	0.06	0.02	0.004
Error	0.9	0.6	0.3	0.07	0.03	0.006
8 µm- Z %	0.1 phr	1 phr	10 phr	25 phr	50 phr	100 phr
Average	97.9	97.5	98.4	99.55	99.7	99.83
Standard deviation	0.5	0.8	1.02	0.07	0.1	0.03
Error	0.6	0.9	1.3	0.08	0.1	0.04
38µm- Z%	0.1 phr	1 phr	10 phr	25 phr	50 phr	100 phr
Average	97.8	97.2	95.4	91.5	90.4	92.2
Standard deviation	0.5	0.5	0.7	0.5	0.7	0.4

Table 18 continues here.						
38μm- Z%	0.1 phr	1 phr	10 phr	25 phr	50 phr	100 phr
Error	0.6	0.6	0.9	0.6	0.8	0.5
67μm- Z%	0.1 phr	1 phr	10 phr	25 phr	50 phr	100 phr
Average	98.7	97.4	95.5	95.4	81.1	78.7
Standard deviation	0.2	0.1	0.8	0.4	1.7	1.2
Error	0.3	0.2	1.1	0.5	2.1	1.5

Results were presented on regular ASTM meeting and according to results in Table 18, ASTM committee on their regular meeting decided to prepare samples with Z % range between 80 and 100. Therefore 3 types of sample were chosen to be prepared- GS of sizes 8 μm, 38 μm and 67 μm. All in dosing of 50 phr to SR.

10.4 Preparation process of calibration object with 50 phr of GS

Preparation process does not require any special equipment or handling. Common laboratory equipment is necessary, i.e., weighing machine, glass beaker of 250 ml, stirrer, hot air oven (dryer), vacuum oven (dryer), etc. Table 19 summarize mixture composition of calibration objects.

Table 19- Mixture composition of samples with GS

	phr	weight/ g	density/ g.cm^{-3}	weight %
Rubber matrix	100	20	1.1	62.5
Curing agent	10	2	1.03	6.25
GS	50	10	2.6	31.25

Preparation process of calibration object began with the stirring of SR with GS for 10 minutes in a glass beaker. The rotation speed is 300 revolutions per minute (rpm). After 10 minutes, the curing agent is added and whole compound is mixed for another 5 minutes. Total mixing time is therefore 15 minutes. Then the compound is poured into a steel rounded mold with diameter of 55 mm and thickness 12.5 mm. Next step is the deaeration for 30 minutes in vacuum oven (dryer), because it is very important to remove all air bubbles from the compound as they can negatively influence the measurement. Last step is the crosslinking. The sample was put into hot air oven (dryer) and cured for 2 hours at 80 °C. Example of clear silicone rubber reference object is displayed in Figure 24.

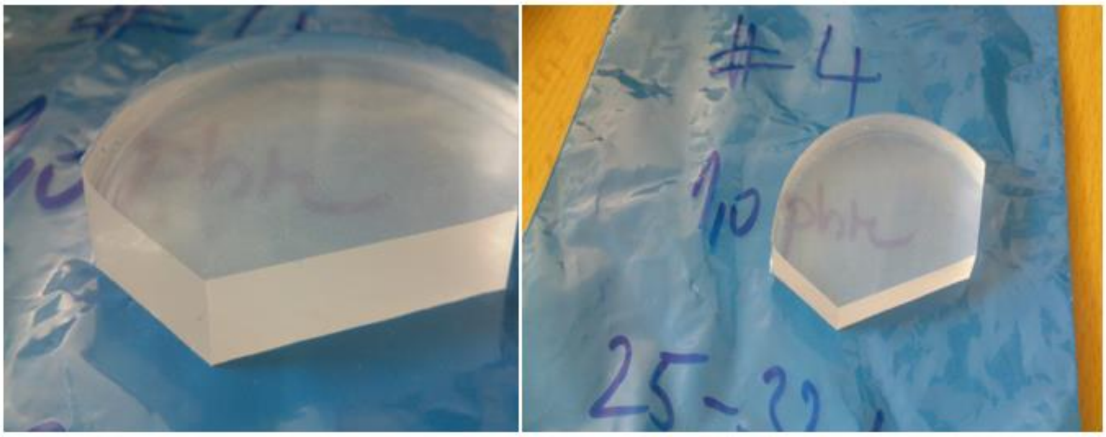


Figure 24- Clear calibration object

10.5 Pigment evaluation

Another step in the calibration object preparation was finding of suitable pigment for sample colouration, which does not have significant influence on the OD measurements. The reason for colouration is that potential customers of the calibration object desire coloured object, not a clear one. Several pigments such as black acrylic colour, ink carbon black, black and red tempera colour were considered as potential pigments for reference object. These pigments were considered due to their availability, price and colour. Examples of different pigments in silicone rubber are displayed in Figures 25 and 26.

Figure 25- Examples of different pigments mixed with SR

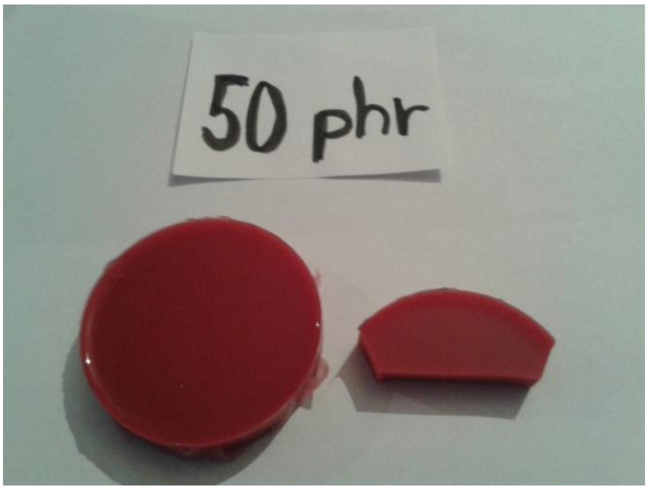


Figure 26- Calibration object with 50 phr of GS and pigmented by red tempera

Each pigment was added to the silicone rubber and sample was cross-linked. The amount of pigment added into mix was 2 phr, which is 0.4 grams. Instead of mixing SR with GS, SR is mixed only with pigment for 10 minutes and then is added the curing agent and everything is mixed altogether for 5 minutes, so mixing time is 15 minutes. Same mold is used. The samples did not contain any fillers.

Then the SR with pigments was compared with clear SR. In this case the compared value was Z value instead of dispersion degree, because the samples were unfilled as mentioned before. Measurements were performed on OD. From each sample there was made one cut with thickness 5 to 10 mm and each cut was placed in front of the testing window and scanned 5×. This scanning was repeated 10× for each sample and mean dispersion values were obtained for each pigment.

The compared value was Z value and the results are shown in Table 20 and Figure 27.

Table 20- Pigment evaluation

Z value %	Clear SR (1)	Red tempera (2)	Black acrylic colour (3)	Black tempera (4)	Ink carbon black (5)
Average	100.0	99.5	95.1	92.8	86
Standard deviation	0.1	0.2	1.1	0.7	5
Error	0.1	0.1	0.8	0.5	3

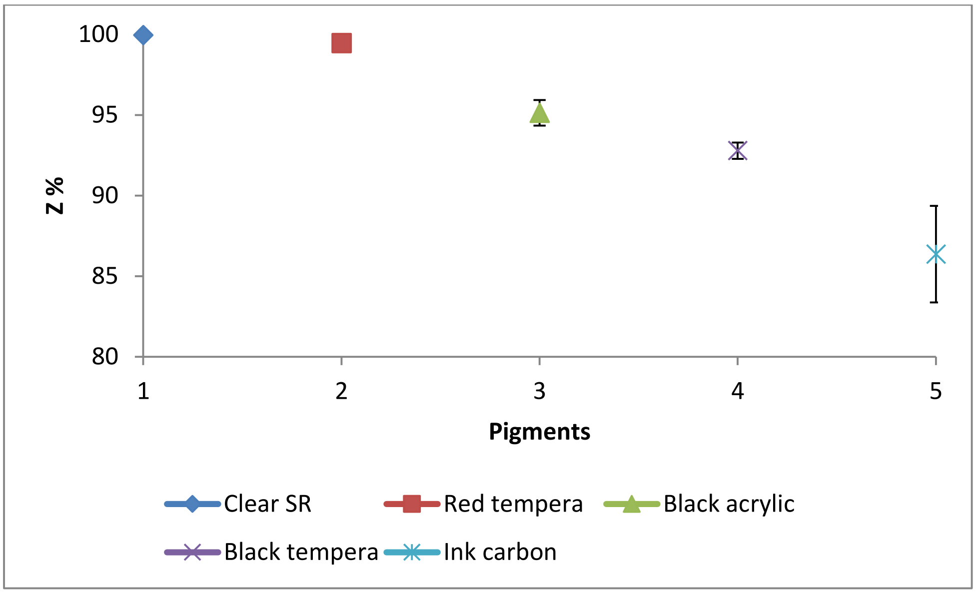


Figure 27- Pigment evaluation

According to results and graphical results, certain similarity is observed in values for clear SR and SR with red tempera. The biggest error of measurement is observed with Ink carbon sample. Statistical significance of the result were analysed with ANOVA.

Zero hypothesis: Pigment does not have any significant influence on measurement.

$$H_0: \sigma_F^2 = 0 \tag{20}$$

The alternative hypothesis says the opposite, pigment has an influence.

$$H_1: \sigma_F^2 > 0 \tag{21}$$

Table 21- Sampling, groups and degrees of freedom for pigment evaluation

Sampling - N	50
Groups - G	5
Degrees of freedom among the groups- G − 1	4
Degrees of freedom within the groups- N − G	45
Probability of error - α	0.05

Table 22- ANOVA for pigment evaluation

	Sum of the square deviations	Degrees of freedom	Mean square (variance estimate)
Variability among the groups	1236	G-1= 4	309
Variability within the groups	227	N-G= 45	5
Tested value	62		
Critical value	3		

Zero hypothesis is rejected and pigment has an influence on the measurement. For further investigation when there is any group, which does not have influence on measurement was exploited the Scheffé´s method of comparison [52].

Table 23- Scheffé´s method of comparison for pigment evaluation

Compared groups	$\lvert \bar{X}_n - \bar{X}_k \rvert$	$\sqrt{\frac{G-1}{N-G}.SS_W.F_{critical}.\left[\frac{1}{N_n}+\frac{1}{N_k}\right]}$
Clear SR/ Red tempera	0.5	3.2
Clear SR/ Black acrylic colour	4.8	3.2
Clear SR/ Black tempera	7.2	3.2
Clear SR/ Ink carbon black	13.6	3.2

Scheffé´s method showed, that there is one group which does not have significant influence on the measurement and it was SR with red tempera pigment.

Then preparation process of pigmented calibration object with GS is following:

1. Mixing of pigment with silicone rubber for 10 min.
2. After 8 min of the mixing cycle are added GS. The addition is gradual and lasts 2 minutes till the 10th minute is reached.
3. Subsequent addition of curing agent and mixing of compound for another 5 minutes.
4. Deaeration for 30 min in vacuum oven (dryer).
5. Curing at 80 °C for two hours
6. Calibration object is obtained.

10.6 Stability of the reference object

From each sample with GS of sizes 8 μm, 38 μm and 67 μm one cut was made and this cut was remained preserved during the experiment duration. The stability of the pigmented reference object was measured in time. First measurements were proceeded on the day of cutting, then other measurements were done after one week, after two weeks and lastly after one month from the day of cutting. Table 24 summarize the D % values results and the Table 25 summarize the Z value results compared in time. Measurement were proceeded with OD.

Table 24- D % results of stability of the calibration object

D %	1st measurement cutting day	After one week	After two weeks	After one month
Average SR + 8 μm GS	100	100	100	100
Standard deviation	0	0	0	0
Error	0	0	0	0
Average SR + 38 μm GS	99.73	99.71	99.73	99.66
Standard deviation	0.1	0.1	0.06	0.1
Error	0.05	0.05	0.03	0.05
Average SR + 67 μm GS	96.4	96.4	96.3	96.1
Standard deviation	0.4	0.3	0.2	0.3
Error	0.2	0.1	0.1	0.2

Table 25- Z% results of stability of a calibration object

Z %	1st measurement cutting day	After one week	After two weeks	After one month
Average SR + 8 µm GS	99.79	99.76	99.6	99.78
Standard deviation	0.05	0.07	0.2	0.05
Error	0.02	0.03	0.1	0.02
Average SR + 38 µm GS	93.5	93.5	93.65	93.3
Standard deviation	0.3	0.3	0.2	0.4
Error	0.2	0.1	0.08	0.2
Average SR + 67 µm GS	89.2	89.3	89.19	89.0
Standard deviation	0.5	0.3	0.2	0.4
Error	0.2	0.2	0.09	0.2

Results showed that calibration object after one month is stable. The average values are spread within the same confidence intervals according to measurement errors. Also from the macroscopic observations during one month from the cutting, the samples neither changed its colour, shape, nor degrade. Thus, stability was evaluated as high.

10.7 Comparison of the results with the OD and new dispergrader (ND)

The calibration object was compared on both devices, Dispergrader$^+$ (OD) and Dispergrader α-view (ND). The samples were measured on ND with different exposure times, i.e. 10 ms, 20 ms, 40 ms and 50 ms to obtain comparable results. Therefore results are not very satisfactory, because it was observed, that the devices show different results in all cases of calibration object samples, especially with the GS of 38 and 67 μm as can be seen Tables 26 and also in Figure 28.

Table 26- Comparison of OD and ND for 8 μm GS

SR + 8 μm GS					
D %	OD (1)	ND 10 ms (2)	ND 20 ms (3)	ND 40 ms (4)	ND 50 ms (5)
Average	100	99.91	99.9	99.76	98.98
Standard deviation	0	0.02	0	0.05	0.04
Error	0	0.01	0	0.02	0.02
SR + 38 μm GS					
D %	OD	ND 10 ms	ND 20 ms	ND 40 ms	ND 50 ms
Average	99.73	96.53	95.14	91.76	90.48
Standard deviation	0.11	0.17	0.08	0.09	0.07
Error	0.05	0.08	0.04	0.04	0.03
SR + 67 μm GS					
D %	OD	ND 10 ms	ND 20 ms	ND 40 ms	ND 50 ms
Average	96.4	89.6	88.17	86.21	84.35

Table 26 continues here.					
SR + 67 µm GS					
D %	OD	ND 10 ms	ND 20 ms	ND 40 ms	ND 50 ms
Standard deviation	0.4	0.1	0.1	0.1	0.1
Error	0.2	0.1	0.03	0.05	0.05

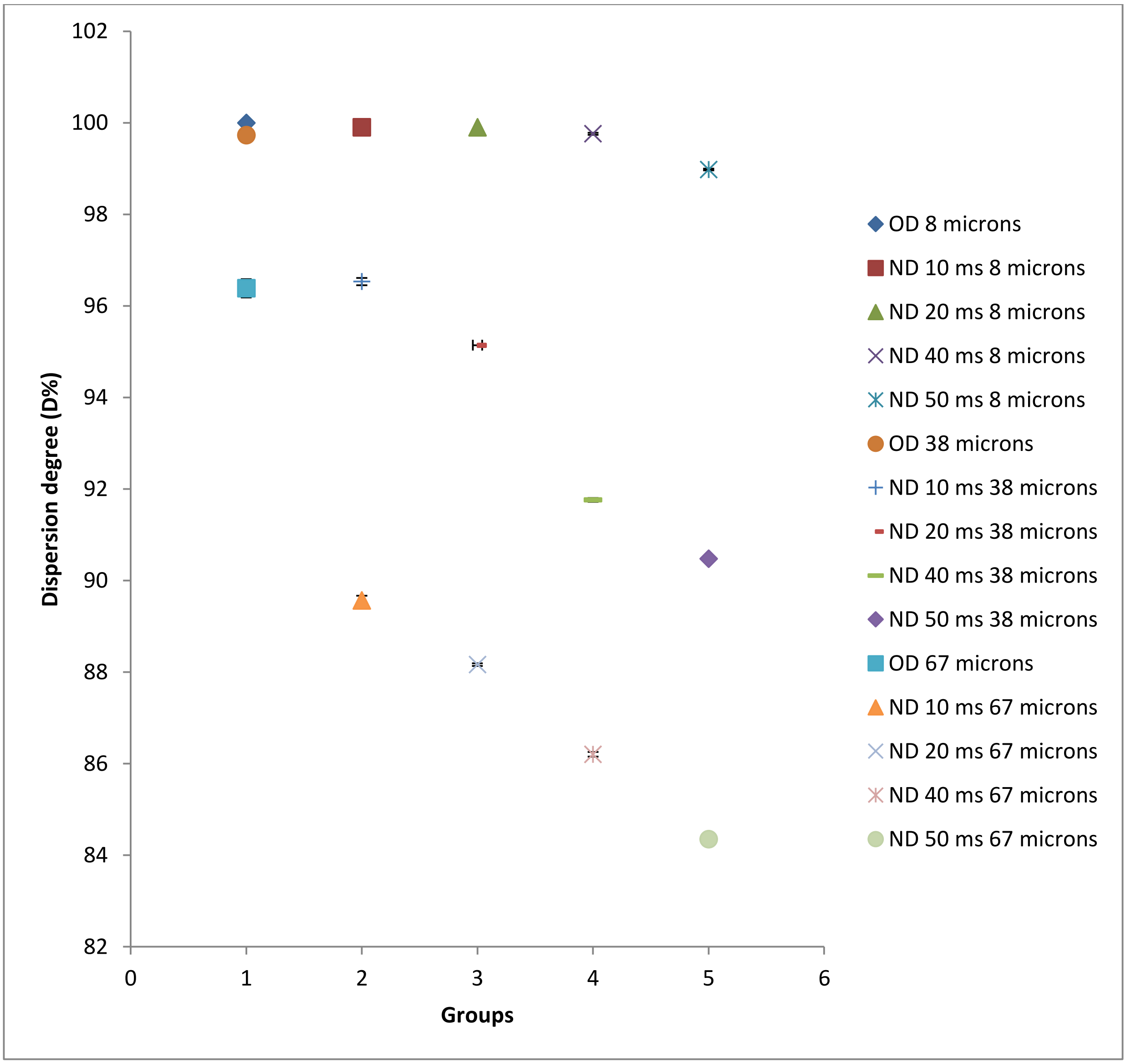


Figure 28- Comparison of SR+ GS on OD and ND

The most similar results were observed with the calibration object with GS of 8 µm with the exposure times on ND set as 10 ms and 20 ms. Eventually, ND with 40 ms exposure time can also be comparable with the OD results from the graphical explanation in Figure 30. The result of ND with 50 ms exposure time is obviously different and not comparable with the other results from GS 8 µm.

The differences between devices for the calibration objects with 38 µm and 67 µm GS are higher than in the first calibration object with 8 µm GS. Even from the graphical explanation in the Figure 30, it is obvious that the results are not comparable and the differences among the results are higher than it was expected.

11 IMPACT OF THE MEASUREMENT DEVICE SETTING

11.1 Exposure time

Exposure time means the exposure time of the camera used during tests. The evaluation was proceeded on ND to investigate, whether the exposure time has any influence on measurements. The assumption regarding the exposure time is that the shorter exposure time the higher dispersion value and vice versa the longer exposure time the lower dispersion value is.

For exposure time were chosen two CB samples with different dispersion values; sample 1- 99% and sample 2- 47%. Samples were provided by Continental Reifen Deutschland GmBH. And investigated exposure times were chosen as follows:

10 ms, 20 ms, 40 ms, 50 ms, 60 ms, 80 ms, 160 ms, 320 ms, 640 ms and 1280 ms. From each sample was made one cut, this cut was scanned 5× at different places on the surface and this scanning was repeated with each exposure time 10×. And also one image from each evaluation was stored as a reference. Results are summarized in following Table 27.

Table 27- Exposure time with CB sample with D = 99%

D = 99%										
	10 ms	20 ms	40 ms	50 ms	60 ms	80 ms	160 ms	320 ms	640 ms	1280 ms
Average	99.9	99.6	99.11	99.0	98.81	98.89	98.5	97.4	99.89	100
Standard deviation	0	0	0.03	0	0.1	0.03	0.1	0.2	0.03	0
Error	0	0	0.02	0	0.04	0.02	0.1	0.2	0.02	0

Results from Table 27 were firstly macroscopically compared as Images 29 and 30, whether there is any similarity among them. Each exposure time has assigned one image.

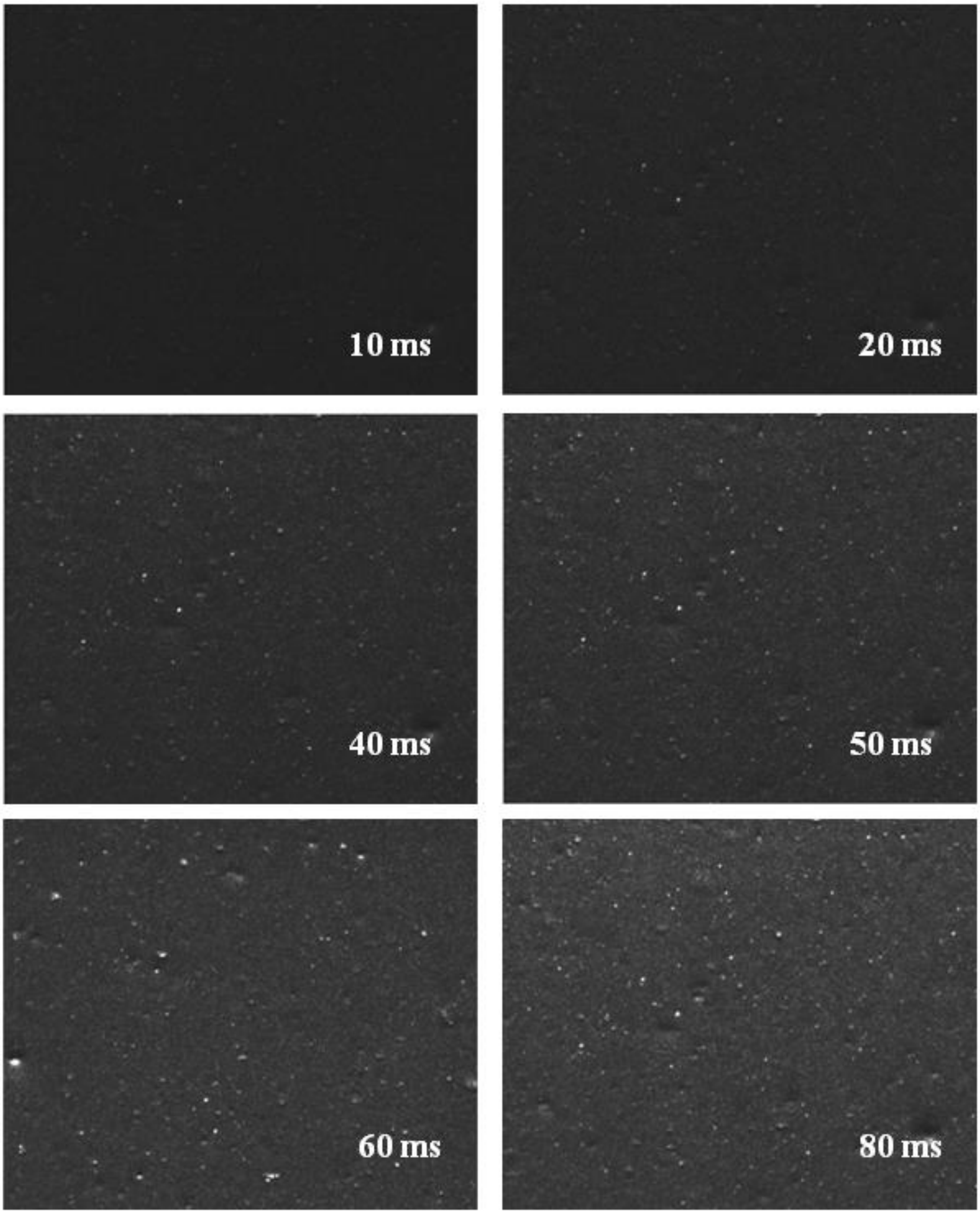


Figure 29- Exposure time 10 – 80 ms for D = 99 %

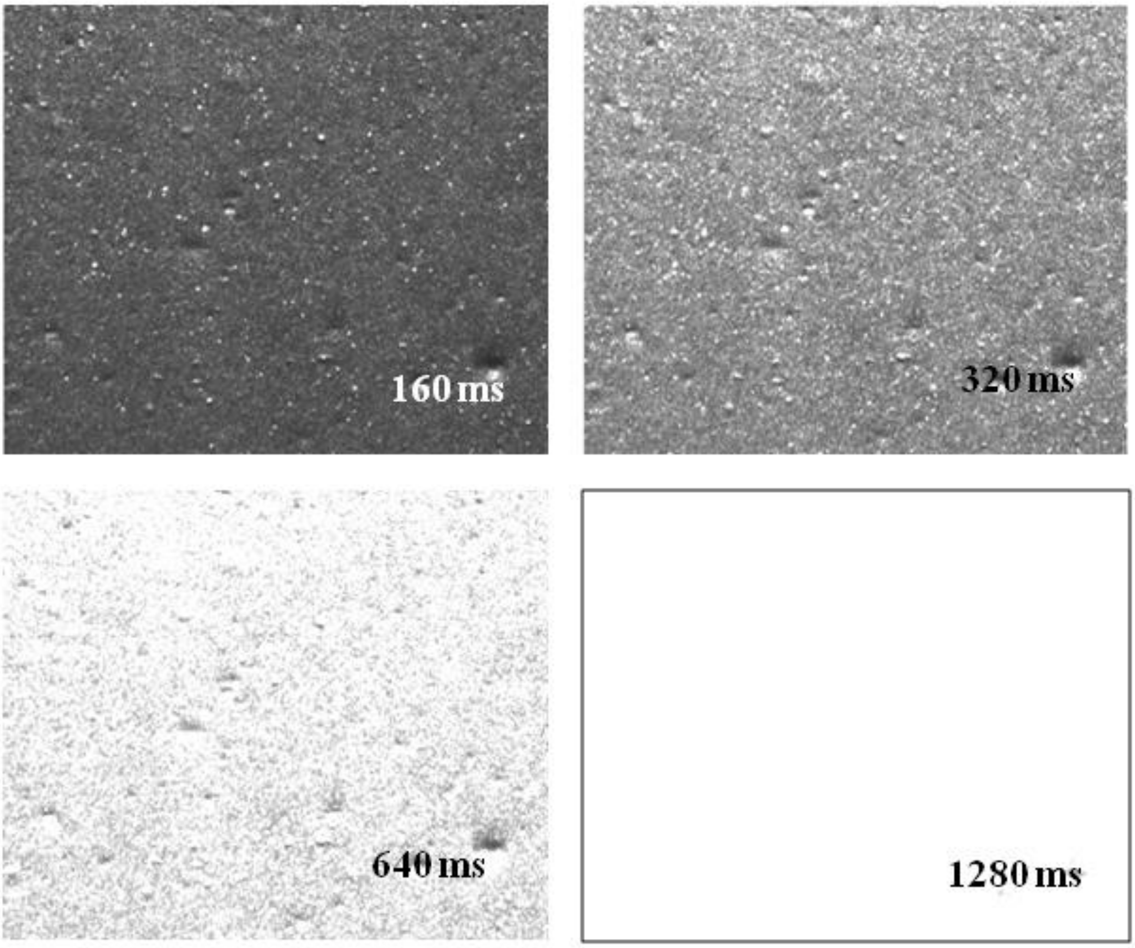


Figure 30- Exposure time 160 – 1280 ms for D = 99 %

The lower exposure times shows darker resulting images than the higher exposure times. It is obvious, that Images with exposure time 640 ms and 1280 ms are overexposed. They are white, but CB compound is not a white compound, therefore these two exposure times are not recommended for the measurements. The results are definitely not relevant. There is observed certain similarity between exposure times 40 ms to 80 ms with an eye observation. It could indicate, that there is not significant difference between the exposure times, but this assumption was further proved by ANOVA. The Figure 30 also showed that there is a specified exposure time limit, between 320 ms and 640 ms, from where the results are being irrelevant, because Dispergarder evaluated the CB as the white compound, because the sample is exposed for a long time as was mentioned before.

Table 28 demonstrates the limit investigation for sample with D = 99% and the limit was found at 400 ms, so anything more than 400 ms is not relevant exposure time, because the device starts to evaluate the overexposed compounds as white compounds.

Table 28- Limit investigation of sample with D = 99 %

Limit investigation, sample with D = 99%													
ms	10	20	40	50	60	80	160	320	400	500	600	640	1280
D%	99.9	99.6	99.1	99	98.8	98.9	98.5	97.4	97	97.8	98.2	99.9	100

Therefore ANOVA evaluation was applied to exposure times from 10 ms to 320 ms.

Table 29- ANOVA for sample with D = 99 %

D = 99 %	Sum of square deviations	Degrees of freedom	Mean square (variance estimate)
Variability among the groups	39.4	G-1 = 7	5.6
Variability within the groups	0.5	N-G = 72	0.007
Tested value	800		
Critical value	2.1		

According to ANOVA evaluation, the exposure time has an influence on measurement. For investigation whether there are exposure times without difference between them was used Scheffé´s method of comparison included in Table 30 [52].

Table 30- Scheffé´s method of comparison for sample with D = 99 %

Compared groups	$\lvert\bar{X}_n - \bar{X}_k\rvert$	$\sqrt{\frac{G-1}{N-G}.SS_W.F_{critical}.\left[\frac{1}{N_n}+\frac{1}{N_k}\right]}$
10 ms/20 ms	0.3	0.14
20 ms/40 ms	0.5	0.14
40 ms/ 50 ms	0.11	0.14
40 ms/ 60 ms	0.3	0.14
40 ms/ 80 ms	0.2	0.14
50 ms/ 60 ms	0.19	0.14
50 ms/ 80 ms	0.11	0.14
80 ms/ 160 ms	0.4	0.14

It was proved that there is no significant difference between exposure times 40 ms and 50 ms, as well as exposure times 50 ms and 80 ms. Thus, the assumption from the macroscopic observation that all exposure times between 40 to 80 ms are not significantly different was not confirmed.

Table 31- Exposure time with CB sample with D = 47 %

D = 47%										
	10 ms	20 ms	40 ms	50 ms	60 ms	80 ms	160 ms	320 ms	640 ms	1280 ms
Average	90.1	68.6	49.7	47.6	44.2	45.2	40.5	37	98.45	100
Standard deviation	0.1	0.2	0.3	0.4	0.6	0.8	6.5	5.7	0.1	0

Table 31 continues here.

	10 ms	20 ms	40 ms	50 ms	60 ms	80 ms	160 ms	320 ms	640 ms	1280 ms
Error	0.1	0.2	0.2	0.3	0.4	0.6	4.6	4.1	0.04	0

The same macroscopic image comparison was proceeded with CB sample with D = 47%. And the same patterns were observed as in the case of sample with D = 99%. Lower exposure times showed darker resulting images as seen in Figures 31 and 32. Also there was investigated a limit, from which results are irrelevant and results are included in Table 32. The border is 325 ms. Higher exposure time is not recommended for measurements.

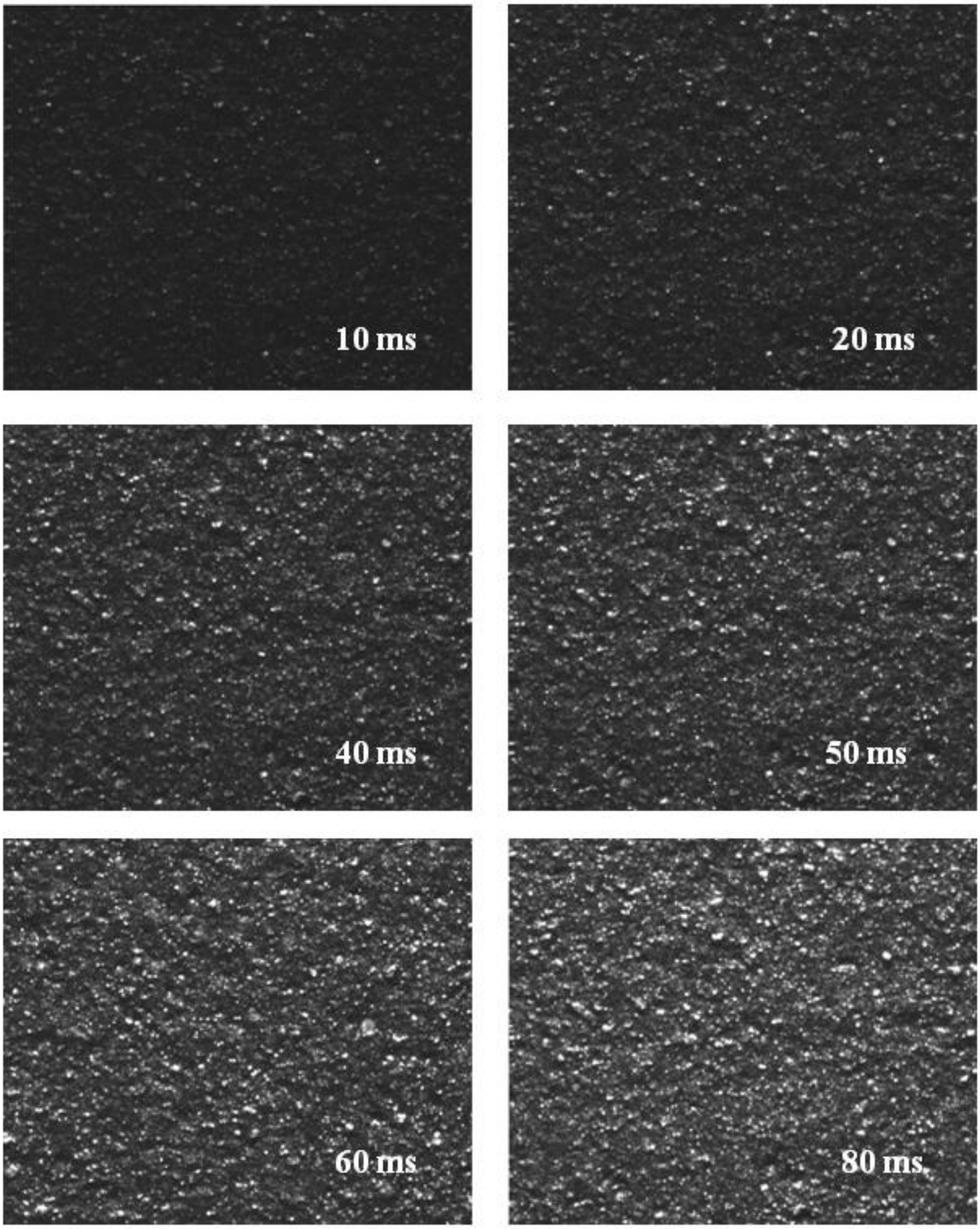


Figure 31- Exposure time 10 – 80 ms for D = 47 %

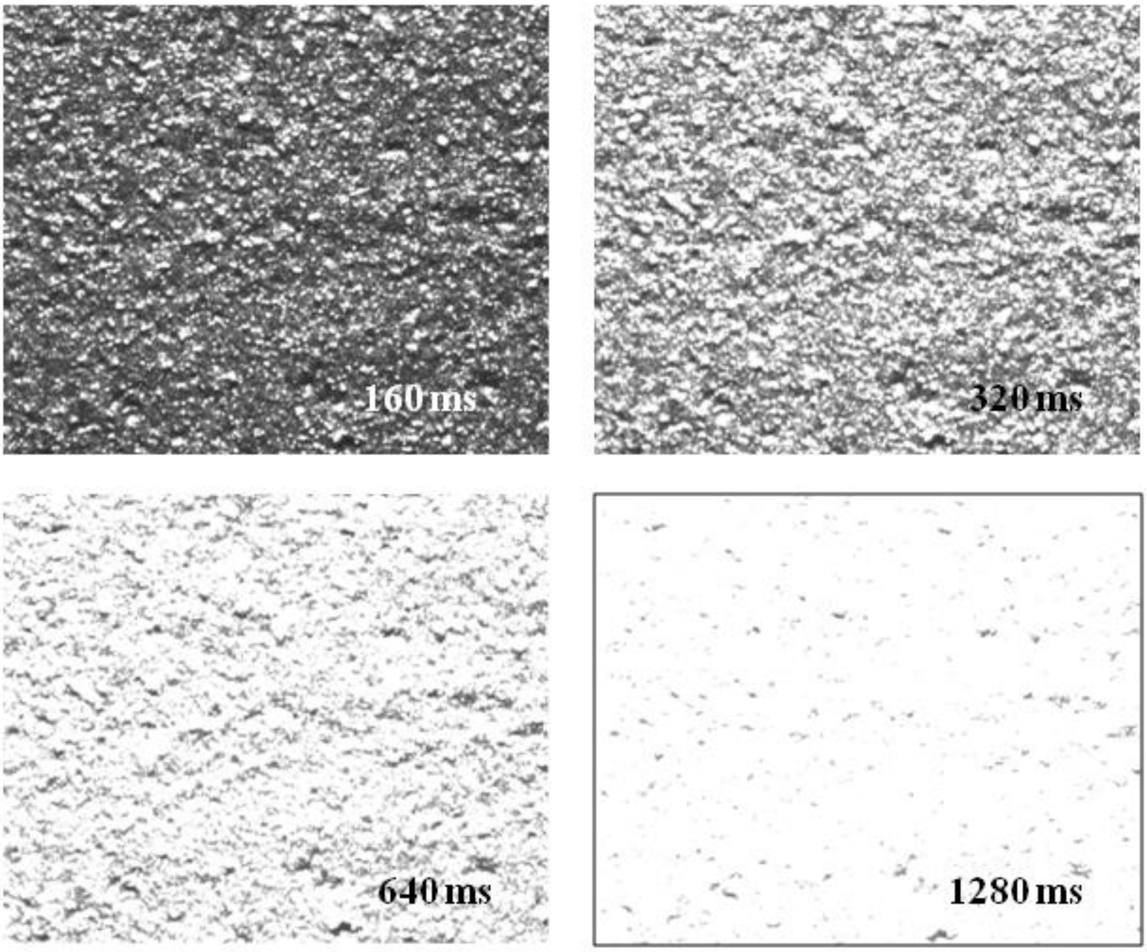


Figure 32- Exposure time 160 – 1280 ms for D = 47 %

Table 32- Limit investigation of sample with D = 47 %

Limit investigation, sample with D = 47 %													
ms	10	20	40	50	60	80	160	320	325	350	400	500	600
D%	90.1	68.6	49.7	47.6	44.2	45.2	40.5	37	35.4	43.5	61.3	97.8	98.9
ms	640	1280											
D%	98.5	100											

The limit for sample with D = 47 % was found at 325 ms. Higher exposure times provide overexposed and not relevant images and results.

Table 33- ANOVA for sample with D = 47 %

D = 47 %	Sum of square deviations	Degrees of freedom	Mean square (variance estimate)
Variability among the groups	22119	G-1 = 7	3159
Variability within the groups	681	N-G = 72	9.4
Tested value	336		
Critical value	2.1		

Table 34- Scheffé´s method of comparison for sample with D = 47 %

Compared groups	$\|\bar{X}_n - \bar{X}_k\|$	$\sqrt{\frac{G-1}{N-G}.SS_W.F_{critical}.\left[\frac{1}{N_n}+\frac{1}{N_k}\right]}$
40 ms/ 50 ms	2.1	5.2
50 ms/ 80 ms	2.4	5.2

With method of comparison of Scheffé was proved that there is no significant difference between exposure times 40/50 ms and 50/80 ms as in the first case of sample with D = 99 %.

11.2 Threshold for image evaluation

The threshold for image analysis, also referred as threshold for dispersion, is an important setting of the ND device. Two standards, ISO 11345 [37] and ASTM D7723 [35], describe the threshold for image analysis with two different values. In ISO 11345 [37] is threshold set as 23 µm and it means that agglomerates with sizes smaller than 23 µm are ignored and not taken into calculation. The current ASTM D7723 [35] requires the threshold value as 5 µm, so only agglomerates smaller than 5 µm are ignored. This investigation was done to show, whether the setting of threshold for image evaluation with specific value has an influence on the measurements or whether there is no significant influence and it does not matter, whether the dispersion threshold is set to 23 µm or 5 µm.

Measurements were proceeded on the NDw. There were chosen two samples with CB, one with dispersion value 99 % and the other one with the dispersion value of 57 %. One cut was made from each sample and this cut scanned 5× at different places of the surface and the scanning procedure was repeated 10× with the dispersion threshold 23 µm and also 10× with the dispersion threshold 5 µm.

In the Table 35 there are included all results from the measurement for both thresholds and both samples with D = 99 % and D = 57 %.

Table 35- Investigation of the dispersion threshold for sample with 99 % and 57 % dispersion value

D = 99 %	5 µm (1)	23 µm (2)
Average	92.0	99.17
Standard deviation	0.1	0.1
Error	0.1	0.05
D = 57 %	5 µm	23 µm
Average	28.0	57.6
Standard deviation	0.2	1.5
Error	0.1	1.1

Graphically is Table 38 displayed in following Figure 33. There is observed a difference among the values.

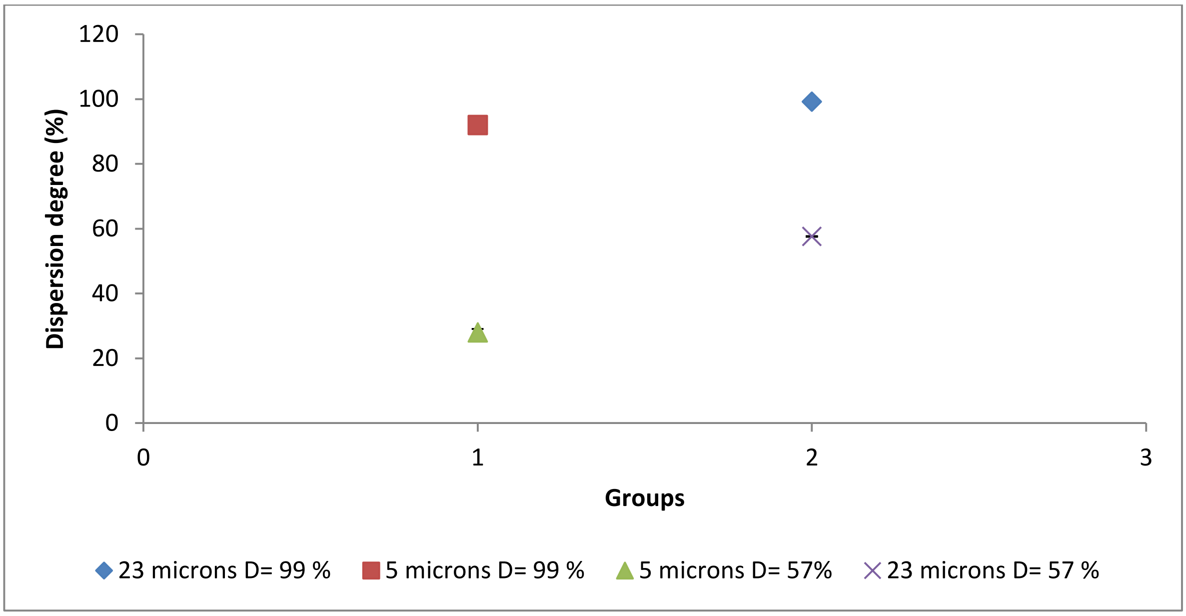


Figure 33- Dispersion threshold evaluation for both samples

Zero hypothesis is formulated as follows, the threshold for image analysis does not have any significant influence on the measurement:

$$H_0: \sigma_F^2 = 0 \tag{22}$$

The alternative hypothesis say, that the threshold for image analysis has an influence on the measurement:

$$H_1: \sigma_F^2 > 0 \tag{23}$$

Table 36- Sampling, groups and degrees of freedom for sample D = 99 %

Sampling - N	20
Groups - G	2
Degrees of freedom between the group- G – 1	1
Degrees of freedom within the group-	18

N – G	
Table 39 continues here.	
Probability of error - α	0.05

Results were also analysed with ANOVA and the results of ANOVA are included in Table 37.

Table 37- ANOVA for sample with high dispersion value

D = 99%	Sum of the square deviations	Degrees of freedom	Mean square (variance estimate)
Variability between the groups	259	G-1=1	259
Variability within the groups	0.1	N-G=18	0.006
Tested value	43167		
Critical value	4		

The tested value is higher than critical one in this case, the zero hypothesis is rejected. Thus, the threshold for image analysis has an influence on the measurement.

For the sample with D = 57% are hypotheses the same as for the sample with D = 99% and the values of sampling, degrees of freedom, etc. are included in Table 36.

For sample with low dispersion value there is observed noticeable difference between both thresholds than in the first case with the sample with higher dispersion value. The dispersion value with 5 μm threshold is almost twice smaller than the dispersion value with 23 μm.

Table 38- ANOVA for sample with low dispersion value

Dispersion value 57%	Sum of the square deviations	Degrees of freedom	Mean square (variance estimate)
Variability among the groups	4381	G-1=1	4381
Variability within the groups	22	N-G=18	1.2
Tested value	3651		
Critical value	4		

So according to results of samples with high and low dispersion values, it is important to decide which threshold is suitable for specific application. The threshold of 23 µm complies with both standards and it is used in both devices, OD and ND. Nevertheless, the ignoration of all agglomerates smaller than 23 µm can cause worse resolution, because the agglomerate size ranges already from 2 µm.

12 COMPARISON OF THE DEVICES

OD and ND are two devices, supplied by Alpha Technologies, for macro-dispersion evaluation. Specifications and differences between devices are listed in Table 39. The main aim of the investigation was to find out, whether these two devices are comparable and whether the transition from measurements with OD to measurements with ND is possible and the obtained results are comparable.

Table 39- OD and ND specification

Specifications	OD	ND
Electrical requirements	80-250 VAC, 47-63 Hz, 2 Amps	80-250 VAC, 47-63 Hz, 4 Amps
Dimensions	Height: 279.4 mm Width: 165.1 mm Depth: 539.75 mm	Height: 200 mm Width: 296 mm Depth: 478.5 mm
Magnification/ Resolution	30x, 100x	Standard = 3 µm High = 1 µm
Image processing/analysis	Digital	Digital
Picture format	BMP	BMP, JPG, PNG
Test specimen	30x: minimum size 10 x 8 mm 100x: minimum size 4.5 x 4 mm	minimum size 12.5 x 6.5 mm
International standards	ISO 11345	ISO 11345 ASTM D7723
Measurement	Manual scanning capabilities	Automatic and manual scanning capabilities

Table 39 continues here.

Specifications	OD	ND
Autofocus	No	Yes
Lighting system	One position LED	Four position LED
Software	DisperData	Enterprise
White compound evaluation	No	Yes
Stores	Histograms, data and images	Histograms, data and images

For evaluation were chosen two CB samples with D = 99% and D = 55%. With the default setting from the manufacturer, both devices showed different results as seen in Table 40. Therefore the aim of this investigations was to find setting for comparable results of both devices. The dispersion threshold was not chosen setting for comparison, because default value in OD and ND is already 23 µm. Thus, the setting chosen to be investigated was exposure time.

Table 40- Compared results from OD and ND

D = 99 %	OD	ND
Average	99.42	98.7
Standard deviation	0.2	0.3
Error	0.08	0.1
D = 55 %	OD	ND
Average	54.8	47.7
Standard deviation	0.7	0.4

Table 40 continues here.		
D = 55 %	OD	ND
Error	0.3	0.2

The default value of the exposure time for ND is 50 ms, so the range of the exposure times chosen for device comparison was from 10 ms to 50 ms.

Results are listed in Table 41 and graphically displayed in Figure 34.

Table 41- Comparison of the OD and ND with the sample of D = 99 %

D = 99 %	OD (1)	ND 10 ms (2)	ND 20 ms (3)	ND 40 ms (4)	ND 50 ms (5)
Average	99.42	99.85	99.50	98.8	98.7
Standard deviation	0.2	0.1	0.1	0.3	0.3
Error	0.08	0.02	0.05	0.1	0.1

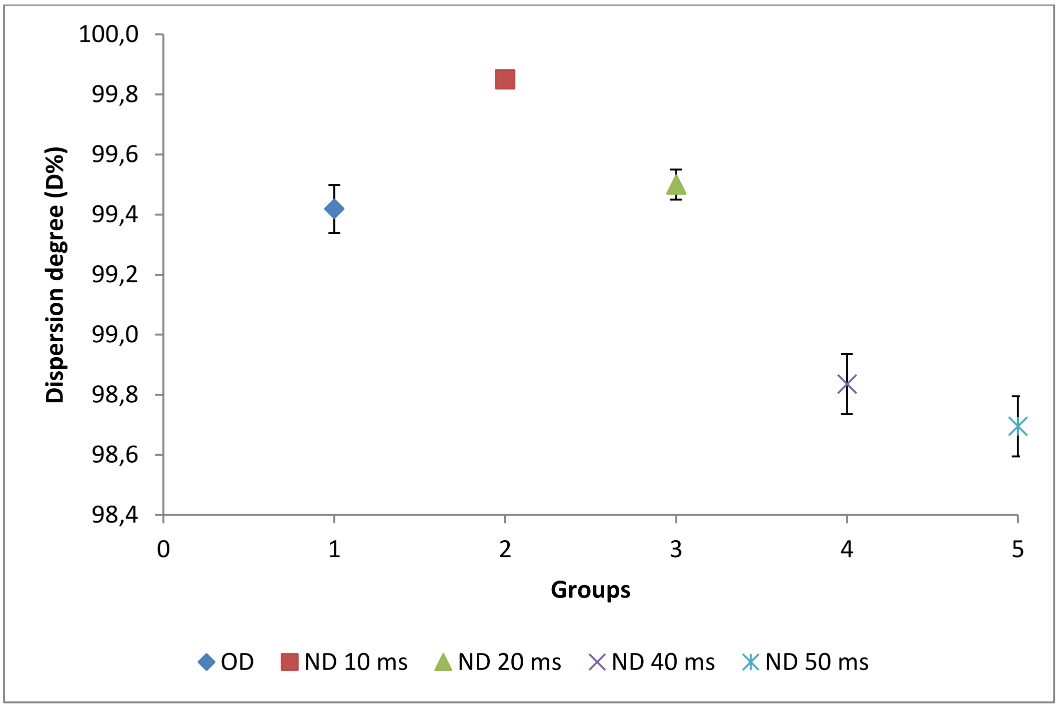


Figure 34- Graphical expression of Table 41

The results were analysed with ANOVA and Scheffé´s method of comparison [52] and the results are listed in Tables 42 and 43.

Table 42- ANOVA of comparison of OD and ND for sample with D = 99 %

D = 99 %	Sum of the square deviations	Degrees of freedom	Mean square (variance estimate)
Variability among the groups	18.6	G-1 = 4	4.6
Variability within the groups	4.2	N- G = 95	0.04
Tested value	115		
Critical value	2.5		

Table 43- Scheffé´s method of comparison for sample D = 99 %

Compared groups	$\lvert\bar{X}_n - \bar{X}_k\rvert$	$\sqrt{\frac{G-1}{N-G}.SS_W.F_{critical}.\left[\frac{1}{N_n}+\frac{1}{N_k}\right]}$
OD/ ND 10 ms	0.43	0.21
OD/ ND 20 ms	0.08	0.21
OD/ ND 40 ms	0.58	0.21
OD/ ND 50 ms	0.72	0.21

It was found that ND with set exposure time on 20 ms can be comparable with the OD.

The following sample and D = 55% was analysed with the same procedure and results can be found in following Tables 44 − 46 and Figure 35. The only difference was added exposure time of 30 ms for broader evaluation of lower D %. Thus, 6 values are compared this time.

Table 44- Comparison of the OD and ND with the sample of D = 55 %

D = 55 %	OD (1)	ND 10 ms (2)	ND 20 ms (3)	ND 30 ms (4)	ND 40 ms (5)	ND 50 ms (6)
Average	54.8	89.4	54.1	52.9	48.8	47.7
Standard deviation	0.7	0.7	0.3	0.1	1.0	0.4
Error	0.3	0.3	0.1	0.1	0.5	0.2

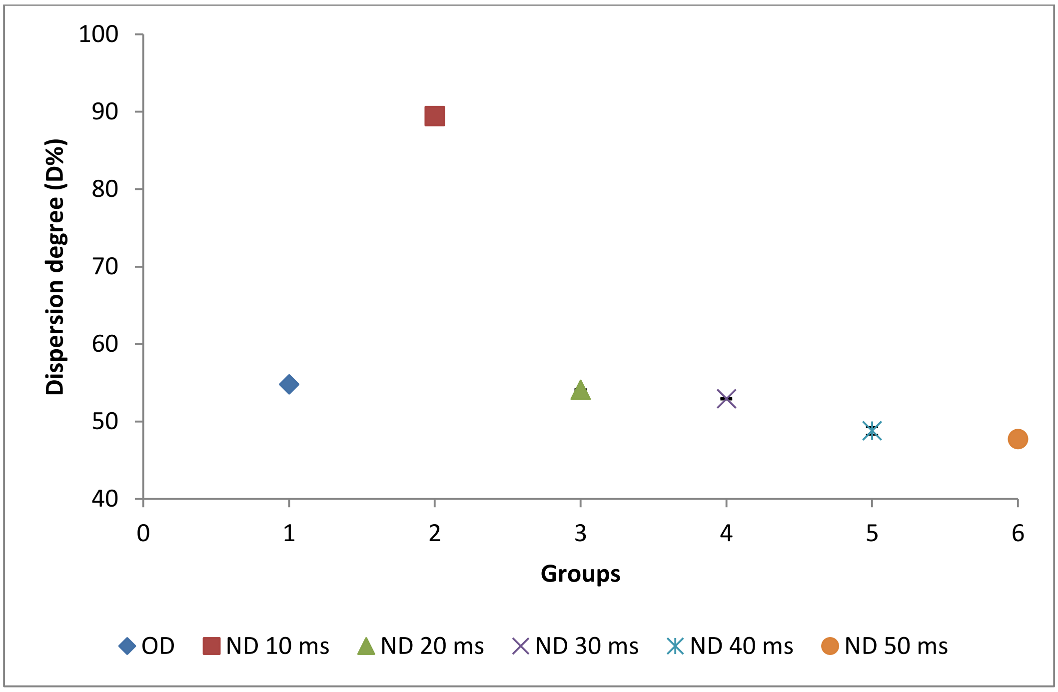


Figure 35- Graphical expression of Table 44

Table 45- ANOVA of comparison of OD and ND for sample D = 55 %

D = 55 %	Sum of the square deviations	Degrees of freedom	Mean square (variance estimate)
Variability among the groups	25415	G-1 = 5	5083
Variability within the groups	82	N- G = 114	0.72
Tested value	7059		
Critical value	2.5		

Table 46-Scheffé´s method of comparison for sample with D = 55 %

Compared groups	$\lvert\bar{X}_n - \bar{X}_k\rvert$	$\sqrt{\frac{G-1}{N-G}.SS_W.F_{critical}.\left[\frac{1}{N_n}+\frac{1}{N_k}\right]}$
OD/ ND 10 ms	0.086	0.131
OD/ ND 20 ms	0.129	0.131
OD/ ND 40 ms	0.904	0.131
OD/ ND 50 ms	1.264	0.131

It was found in all investigated cases that OD is comparable with ND with set exposure time of 20 ms. Nevertheless, this comparison can be applied only in this particular case, because for overall comparison, more ODs would need to be included to a comparison, because each device has its own error. Therefore this is only a suggestion of way how these two devices can be compared.

13 DISCUSSION

The reproducibility of the macro-dispersion evaluation is influenced by measured compound itself therefore CB and silica compounds were investigated for distribution of measured values. Expectation was thesis that broader distribution of measured values is given by lower D %, because the experimental results does not have normal distribution. The thesis was confirmed with the Dispergarder measurements that the lower the dispersion value the broader the distribution of the measured values is. The broadest distributions of measured values were observed with groups of CB with D = 69 % and lower, and with silica/CB compound with D = 74 % and lower. Results were satisfactory. Thus, with the investigation was confirmed that it is not possible to employ CB or silica compounds for calibration object preparation.

The state-of-art chapter 6.1.1. gives the information that the precision statement for the ASTM D7723 [35] is missing, therefore the calibration object is necessary. For further development of the calibration object, made from SR and GS and proposed in Patent CZ 304580 B6 [57], were considered six types of new GS, with different sizes from a different suppliers. Firstly, GS were analysed with the optical microscope and subsequently with image analysis for size distribution. Macroscopical observation with the human eye and then with optical microscope confirmed the spherical shape of the particles as it was expected regarding to their name “spheres”. The image analysis histograms, standard deviations and errors of the measurement proved that GS have narrow size distribution, thus they are appropriate as simulation filler for calibration object. Results were slightly different from the GS manufacturer information. Four suitable types of GS with narrowest size distribution were found. Thus, GS with sizes 3 μm, 8 μm, 38 μm and 67μm from COS Company were then chosen for incorporation into silicone rubber in addition of 0.1, 1, 10, 25, 50 and 100 phr and Z value was measured. Several ranges of Z value from 78 % to 100 % were obtained. Desired range of Z value between 80 and 100 % was suggested by ASTM committee and the best results were obtained with the glass spheres of 8 μm D = 99 %, 38 μm D = 90 % and 67 μm D = 81 % in addition of 50 phr. Therefore these three types of GS were chosen for the preparation of the calibration object, because they provided different Z values in appropriate range. The customer market desires pigmented calibration object and not a clear object, in the next step was necessary to found a suitable pigment that does not have significant influence on measurement. Unfilled silicone rubber was coloured by chosen pigments, i.e. black acrylic colour, ink carbon black, black and red tempera colour and the only investigated pigment that is suitable for preparation of the calibration object was surprisingly red tempera colour, because it was expected that the most appropriate pigment is any black pigment. Unfortunately, the black pigments contained large particles that affected the measurements and D % was obtained even if the SR was unfilled. The calibration object showed good stability according to observations during one month from the cutting day. The results of comparison of calibration object between OD and ND was not satisfactory, because it was found that both devices showed different results, especially in case of GS with size of 38 μm and 67 μm. Thus, expectations that OD and ND shows comparable results with calibration object was not proved. It could be caused by systematical error of the research. Therefore further investigation of this phenomena is required for future development. Nevertheless, the further developed calibration object is valuable and useful tool that helps to increase the reproducibility of the macro-dispersion evaluation.

The exposure time investigations confirmed expectations that this setting has an influence on the measurements and it was proved that with higher exposure time were obtained lower D %, conversely with the lower exposure times were obtained higher D %. Very high exposure times, i.e. 320 ms up to 1280 ms or even higher are not recommended for macro-dispersion evaluation, because with exposure times higher than 320 ms Dispergarder provides overexposed images that are wrongly evaluated as white compounds with higher D %, thus the results are irrelevant. This wrong evaluation is probably caused by the ability of ND to evaluate white compounds and the overexposed images appeared white. The default value 50 ms seems to be optimal value for measurements settings, because there is not any significant difference between 40 and 50 ms or 50 and 80 ms exposure time, therefore default value change is not necessary from the point of view of proceeded investigations. The 40 ms can be recommended in case of time savings, nevertheless difference between 40 ms and 50 ms is not significant and the resolution is the same. Vice versa, 10 ms or 20 ms exposure times are short for macro-dispersion evaluation, because the processing software does not have enough time for the surface evaluation and the resolution is low. Thus, it is necessary to standardize exposure time to obtain reproducible and comparable results.

The value of threshold for image analysis has also an influence on measurement and the again, the expectations were confirmed. The investigation proved that if the threshold for image analysis is set as 23 μm the higher D % is a result, because every agglomerate smaller than 23 μm is ignored and not included into calculation. The disadvantage of the

23 μm threshold is that provided resolution is only standard and it can cause distorted and not accurate results, because agglomerate size is not only higher than 23 μm, but they widely range from 2 μm. Therefore the higher D % is obtained with risk that several significant agglomerates are ignored. The dispersion threshold set as 5 μm decreases this risk, because it only ignores agglomerates smaller than 5 μm. However, the obtained D % are lower than in the case of 23 μm threshold. For the future it is recommended to use only the threshold of 5 μm as included in ASTM D7723 [35], because obtained results have higher resolution and accuracy is also higher.

The aim of the proceeded comparison of the OD and ND was to explore whether the same or comparable results are obtained from both devices, because transition of measurements with OD to measurement with ND is inevitable in the near future. First measurements of comparison of older and new version of Dispergrader showed different results. There was observed significant difference between the obtained D %. It was caused because of the devices were set with the default values and it was demonstrated that it is not the way of comparison, therefore it was necessary to find out what settings need to be changed on the ND to obtain comparable results. The most suitable option appeared the exposure time change, because dispersion threshold in OD has only value of 23 μm. The following exposure times were investigated 10 ms, 20 ms, 40 ms and 50 ms and the expextations for suitable exposure time for comparison were around 10 ms to 20 ms. The default value of the new device is 50 ms thus higher exposure times are irrelevant for this study. It was found that result of both device are comparable only in the case when new device has exposure time set on 20 ms. Thus, first expectation was confirmed. Nevertheless this comparison can be unfortunately applied only in this specific investigation case for two specific devices, because for overall and bigger comparison more devices would be necessary and also other variables such as illumination intensity, light source needs to be considered, but for this specific case the exposure time was enough. Therefore further investigations could be recommended as a project for PhD. studies or manufacturer investigation.

CONCLUSIONS

The aims of the studies were further developing of calibration object, investigation of measurement device settings for increased reproducibility and recommendation how to compare old and new version of Dispergarder device.

The observations of master thesis investigation are summarized as follows.

Calibration object made from the SR and GS is considered as a solution for missing precision statement of ASTM D7723 [35] as it was found that CB or silica compounds have broader distribution of measured values with lower D %. Thus, CB or silica are not suitable for fillers for the creation of calibration object. SR is the proper matrix and GS are appropriate simulating filler because of they narrow size distribution proved by image analysis. Three types of calibration object were finally prepared according to ASTM International requirements. First sample contained 50 phr of GS with size 8 μm, second object 50 phr of 38 μm GS and the third one 50 phr of 67 μm GS. All object were pigmented with red tempera colour as it was found that it is the only pigment that did not significantly influenced measurements, because it contained small particles. The stability of object was proved as high, because they did not changed in a month from the macroscopic and experimental observations. Therefore, calibration object is valuable and useful tool that is designed to improve macro-dispersion evaluation reproducibility.

Two device settings, i.e. exposure time and threshold for image analysis, were analysed for impact of device settings investigation. It was found that both settings have an influence on measurement. With the higher exposure time were obtained lower D % and conversely with the lower exposure times were obtained higher D %. Exposure times higher than 320 ms are not recommended for evaluation, because they provided overexposed and irrelevant results. The most suitable exposure times appear to be 40 ms and 50 ms. The dispersion threshold was analysed according two default values set in two international standards ISO 11345 and ASTM D7723 [35, 37]. For higher accuracy and relevant results is recommended to use 5 μm according to investigated results, but for the measurements in compliance with the OD the 23 μm is necessary.

In the research was also suggested a way how to obtain comparable results from OD and ND. The ND with exposure time set as 20 ms showed comparable results with OD. Unfortunately this comparison is applicable only for one specific case. For overall comparison further investigation is necessary.

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LIST OF ABBREVIATIONS

T_g	Glass transition temperature
ASTM	American Society for Testing and Materials
ISO	International Organization for Standardization
MPTS	3-Mercoptopropyl(trimethoxy)silane
TESPT	Bis(triethoxysilylpropyl)tetrasulfide
Si	Silicone
$SiCl_4$	Silica tetrachloride
H_2	Hydrogen
O_2	Oxygen
HCl	Hydrochloric acid
SSA	Specific surface area
BET	Braunner- Emmet- Teller
m^2	square meter
g	gram
ml	mililiter
CB	Carbon black
nm	nanometer
SiO_2	silicone dioxide
m	meter
μm	micrometer
DC	direct current
AC	alternating current
MSM	mechanical scanning microscopy
ISO	International Organization for Standardization

ANOVA	Analysis of Variance
SS	sum of squares
SS_B	sum of squares between the groups
SS_W	sum of squares within the groups
SS_T	total sum of squares
dF	degrees of freedom
MS	mean square
MS_B	means square between the groups
MS_W	mean square within the groups
MS_T	total mean square
D%	dispersion value
phr	parts per hundred rubber
rpm	revolutions per minute
SR	Silicone rubber
GS	Glass spheres
COS	Cospheric
PS	Polysciences
OD	Old dispergrader
ND	New dispergrader

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