Study of Influence of Natural Stone Surface Roughness on Wetting Characteristics for the Application of Liquid Coating Systems and on the Adhesive Strength of Thin Epoxy Coatings Over Natural Stone Substrates

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ABSTRACT

In this work, the influence of surface roughness of a natural stone material on two important parameters for the performance of the industrial coating process will be studied. The selected parameters are contact liquid drop angle, to assess the best conditions for the application of the liquid coatings, and the adhesion strength, to assess the best coating performance once the coating has been applied and dried. These two parameters are quantitative and may allow the comparison between different case studies. The study of influence will be addressed in this work from a practical point of view, so that results can be applied in a current industrial process for optimization purposes. The obtained conclusions are expected to be used to propose recommendations for the stone industry to guarantee the performances of the coating systems applied.

KEYWORDS

Natural stone, surface engineering, coatings, adhesion strength, wetting contact angle, roughness.

INTRODUCTION

In the current Natural Stone industrial sector, applying polymeric resins over the surface of natural stone slabs has become a very common task. The main objectives of the resin treatment are, on the one hand, the filling and sealing of natural cavities and, on the other hand, the consolidation of the stone surface to improve its cohesion and avoid problems of surface brokerage. To improve the cohesive effect, the resins are often applied on the back side of the slabs along with a mesh of fiberglass. Many stone materials are resin treated on both their sides (face side and reverse side). Out of many existing chemical families that could be used for this purpose, polyester and epoxy resin are the preferred ones in the natural stone industry [1].

However, in some circumstances these resins present adhesive failures and it is difficult to identify if the problem is derived from an incorrect industrial application, a non optimal state of the initial substrate (surface dirt, moisture and roughness), ageing effects due to environmental factors, an insufficient curing process of the resin or even because the chosen resin is not enough physico – chemically compatible with the natural stone substrate and so a limited adhesion should be expected.

Although some experimental works have been performed to study the mechanical improvements obtained by natural stone materials reinforced by different resin systems, reference [2] can be taken as an example, there is a lack of information in literature about stone surface characteristics and their influence in adhesion processes.

It has been experimentally demonstrated that the adhesion strength of a coating, and therefore the substrate – coating system stability, is influenced not only by the mechanical properties of the

system under test, but also by the nature and preparation of the substrate, the method of coating application, the drying conditions of the coating, the temperature, the humidity and other factors as e.g. the type of the test instrument used [3].

In this work, the influence of surface roughness of a natural stone material on two important parameters for the performance of the industrial coating process will be studied. The selected parameters are the contact liquid drop angle and the adhesion strength.

The contact angle is a measurable physical property to assess the wetting process of a liquid on a substrate. For a liquid to be used as a coating system, a high wettability is recommended, implying that both the substrate and the coating are compatible from a Physicochemical point of view. High wettability systems are those in which contact angle is below 90 degrees, being the ideal perfect wetting state at contact angles of 0 degress. The contact angle is, therefore, a quantitative measurement that can be used to compare different case studies. The physical behavior can also be affected by microscopic surface roughness that can have an effect on localized contact angles. The combinations of contact angle measurements, surface roughness and surface chemical analysis can be used to unambiguously assess the affects of manufacturing process modification and formulation changes improving product performance or reliability of in-line processes such as paint coating, laminate or adhesive systems. Comparing different liquids, the contact angle measurement instantly shows if one liquid 'wets' a surface better than another. In the same way, if the liquid is maintained in the tests, the influence of the substrate can also be studied, which will be the chosen procedure in this experimental work. Surface homogeneity can also be demonstrated using this method. If several drops of known liquid are dispensed onto a surface, differences in contact angles will indicate the degree of inhomogeneity of the surface [4], [5].

On the other hand, the adhesion between the coating, once it has been dried and cured, and the substrate can be taken as a quantitative measurement of the system global stability. The adhesion strength of a coating can be determined by a pull-off test which measures the mechanical resistance of the coating to separation from the substrate when a perpendicular tensile force is applied. The obtained adhesive strength along with the identification of the nature of the adhesive fracture (cohesive or adhesive failure) are the main identifiers of the mentioned coated system stability [6].

There are experimental works in which the influence of roughness has been demonstrated on the adhesive strength of a coating system [7]. That influence appears from a minimum value of surface roughness and makes adhesion strength increase with the increase of roughness surface until a maximum obtainable adhesive strength with a practical rough substrate is reached. One of the objectives of this experimental work is to validate if that effect occurs in the selected system (natural stone substrate and epoxy system) with the different surface roughness values practically attainable in an industrial natural stone polishing line with different abrasive sequences.

1. MATERIALS AND EXPERIMENTAL PROCEDURES

The study will be performed over different samples of a single natural stone material. The chosen material is the limestone known as Crema Marfil, extracted in the Spanish region of Novelda, in the province of Alicante. The choice of this material is justified under the fact that it is a very popular natural stone material at international level and that almost all the material that is processed and elaborated for commercial use in the form of tiles and slabs is treated with chemical resins (polyester and / or epoxy) on both material sides (face side and back side) in order to consolidate the material, to reinforce it and to avoid it being split into small fragments in case of breakage. From the petrography point of view, Crema Marfil is a fossiliferous limestone (bioesparite or grainstone), mainly composed by calcite (99%) but also containing opaques and clay minerals. Its structure is homogeneous and there is evidence of the presence of stylolites, which are serrated surfaces within the rock mass at which mineral material has been removed by pressure dissolution, in a process that decreases the total volume of the rock. The texture of the rock is mainly composed by fossils of protozoa foraminifera, on the microscale and the macroscale, presenting also fragments of red algae and echinoderms.

The chosen coating system is a two component epoxy resin from DOW trade house. The system is composed by a very pure Bisphenol A resin and an aminic hardener in a ratio of 2:1. The fresh mixture has a density of 1.12 g/cm3 and a viscosity of 3,000 cP at 25ºC. The potlife of the mixture is approximately 10 min, which was determined in the laboratory.

Stone samples with different grades of roughness surfaces have been obtained by the application of different sequences of abrasives. In this sense, an industrial polishing line for natural stone with sequential calibrating and polishing heads was used. Eight different samples have been considered, in the form of (30 x 30 x 2) cm tiles, which have been extracted at different points of the polishing line, implying an increasing sequence of the abrasive grains applied (following the FEPA Nomenclature). In table 1, the abrasive sequence is shown and also the points of the polishing line from where each tile was extracted. As mentioned before, the complete sequence goes from coarse to fine abrasives, so that the first abrasives are very aggressive and have the function of grinding and leveling the tiles thickness and the last abrasives remove much less surface material and have the function of generating a polished surface by closing surface porosity. These eight samples represent the different surface roughness states for the natural stone material surface. Each sample was extracted at the output of the abrasive head with which it is related in the table and is numbered according to the sequence of abrasives with which it has been treated. For example, sample 1 was extracted at the output of the first polishing head, implying an initial calibration and a posterior treatment with abrasives of grain 60. In the same way, sample 8 was extracted at the end of the line, implying the treatment with a complete sequence of calibration and polishing heads and a very smooth and glossy surface finish. The polishing line feed rate used was of 1.1 m/min.

Table 1: Abrasive sequence and points of extraction of the samples

Head number	Grain size (FEPA Nomenclature)	Extracted sample
3 calibration heads	-	-
1	60	8
2	80	-
3	120	7
4	220	6
5	320	5
6	340	-
7	400	4
8	600	3
9	800	2
10	Hard abrasive for gloss	-
11	Soft abrasive for gloss	-
12	Cleaning head	1

Each selected tile was cut into smaller samples of (7.5 x 7.5 x 2) cm, to generate the laboratory specimens, and a set of 6 random samples out of a total of 16 were selected, meeting the statistical assumptions proposed in the testing procedures. This composes a total of 8 sets, with 6 specimens in each set.

The complete preparation, coating application and test sequence was applied over all the specimens to guarantee a direct correspondence of the results. The used methodological sequence was as follows:

i. Sample cleaning and surface preparation. The cleaning process was composed by pressured air exposition, a 15 min bath in acetone with ultrasound followed by drying in an oven for 24 h.

ii. Contact angle determination. The chosen liquid for wetting tests was distilled water, instead of the final coating liquid. This decision was made upon the fact that the epoxy coating liquid properties, once the two components are mixed, are highly time dependent and also that the epoxy could leave residues on the surface of the samples. The proposed contact angle test can be considered as an indicator of how surface energy is affected by roughness when a polar liquid drop is applied on the samples surface, but not to determine the real contact angle existing between the samples and the liquid coating resin. The contact angle determination was performed using the standard procedure defined in ASTM D 5725 – 99 [8], determining the contact angle at three times from the drop application: 0.1, 1 and 10s. The test equipment used for conducting angle measurements was an OCA 20LH from Data Physics. One drop was evaluated for each sample and for each set of samples the average values and standard deviations were calculated.

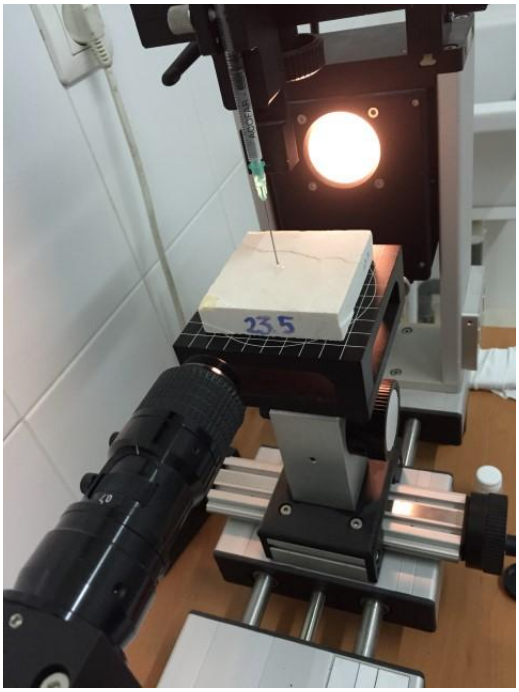


Fig. 1 and 2: Drop Angle measurement equipment (left) and adhesion strength measurement equipment and dolly – sample assembly (right).

iii. Application of coating system and dollies. A total mass of approximately 1g was homogenously manually applied on the surface of the samples using a laboratory rod, implying a coating of 0.15 mm thickness. The samples were previously dried in an oven at 70ºC for a period of 18 h and allowed to achieve an equilibrium temperature in laboratory for 5 h. The coatings were applied at laboratory conditions, complying with the requirements of the standard procedure. Once the coating system was applied, the samples were cured for a minimum period of 24 h before applying the dollies for the adhesive test. According to the adhesive test procedure, 2 cm dollies were glued on the coating surface using the same epoxy resin of the coating system and the minimum possible quantity (around 0.07 g). The obtained assembly was left for resin curing an additional period of 48 hours at laboratory conditions (25ºC and 50% RH).

iv. Determination of the coating adhesion strength by the pull off test. The used procedure for determining the coating adhesion strength over the substrate was the standard procedure defined in ISO 4624-2003 [6] using cylindrical dollies with 2 cm diameter. The used equipment was a portable electronic adhesion tester KN-10 from Neurtek. As the coating thickness was 0.15 mm, the coating was not cut around the dolly diameter. The adhesion strength was determined for each sample and the mean value, the range and standard deviation were

calculated for each set of samples. The nature of the fracture was estimated by means of percentage areas using the following three categories:

- A: cohesive failure of the substrate.
- A/B: adhesive failure between the substrate and the coating system.
- Y/Z: adhesive failure between adhesive and dolly.

No adhesive cohesive failure was identified. Samples with a 100% Y/Z adhesive failure were discarded for statistical analysis, considering that the obtained values were not representative for the coating adhesion strength. For each set of samples the average value of the percentage fracture areas was also calculated. This is not indicated in the standard but was considered as a quantitative way of studying the variation on the type of fracture from one set of samples to the others.

Fig. 3 and 4: Specimens showing a 100% adhesive failure (A/B) on the left and a 100 % substrate cohesive failure (A) on the right.

2. RESULTS

In the following chart the final statistical parameters (mean and standard deviation) of the obtained experimental angles for the distilled water drops at 0.1, 1 and 10 s over each set of samples are shown:

Table 2: Statistical results for contact angle.

SAMPLE 1		
Time [s]	**Mean angle [º]**	**SD Angle [º]**
0.1	69.4	6.2
1	63.5	7.2
10	58.8	4.8

SAMPLE 2		
Time [s]	**Mean angle [º]**	**SD Angle [º]**
0.1	63.2	7.7
1	55.6	5.0
10	53.4	3.8

SAMPLE 3		
Time [s]	**Mean angle [º]**	**SD Angle [º]**
0.1	72.2	15.3
1	68.6	16.1
10	65.7	16.4

SAMPLE 4		
Time [s]	**Mean angle [º]**	**SD Angle [º]**
0.1	66.0	14.3
1	59.3	10.2
10	56.3	9.2

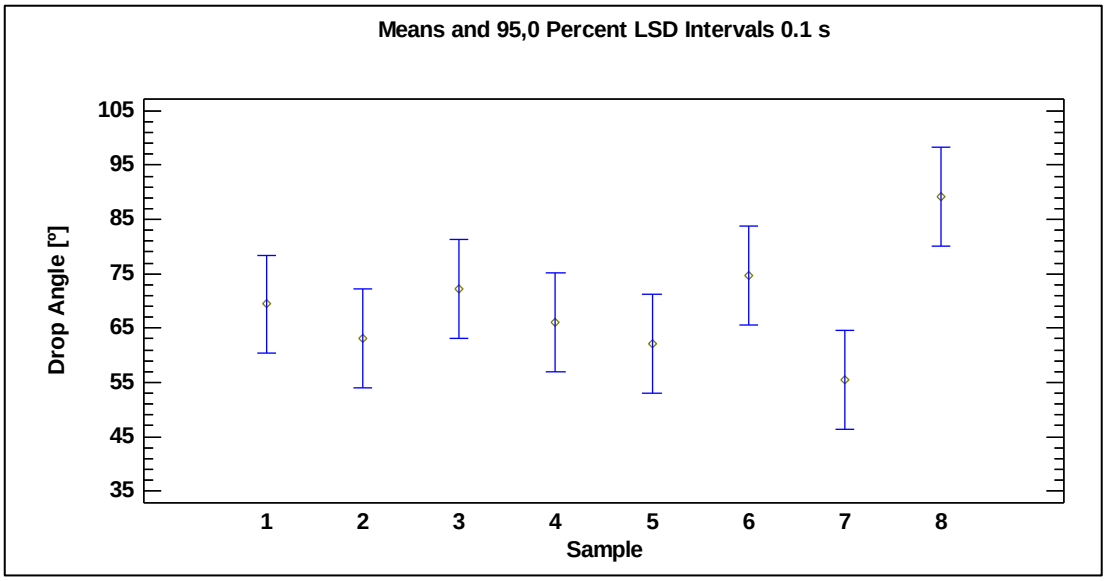
SAMPLE 5		
Time [s]	Mean angle [º]	SD Angle [º]
0.1	62.1	17.5
1	55.0	11.0
10	51.2	9.1

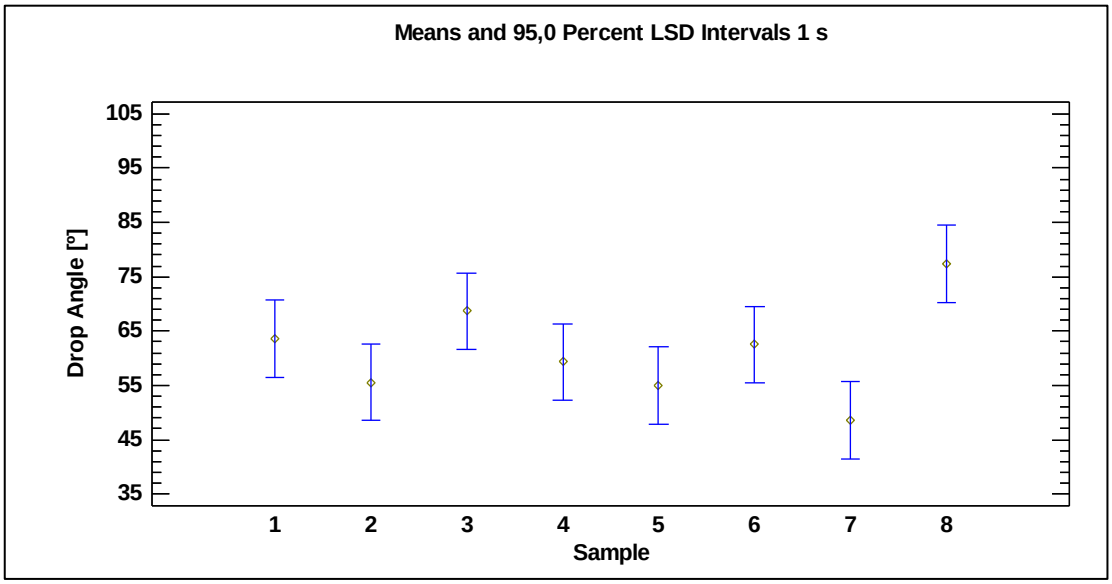
SAMPLE 6		
Time [s]	Mean angle [º]	SD Angle [º]
0.1	74.7	12.1
1	62.5	7.0
10	55.5	7.4

SAMPLE 7		
Time [s]	Mean angle [º]	SD Angle [º]
0.1	55.5	8.6
1	48.6	6.2
10	43.5	6.0

SAMPLE 8		
Time [s]	Mean angle [º]	SD Angle [º]
0.1	89.2	29.4
1	77.4	23.0
10	66.5	16.3

The statistical graphs representative of the six specimens for each sample, summarizing all the data collected, can be also shown:





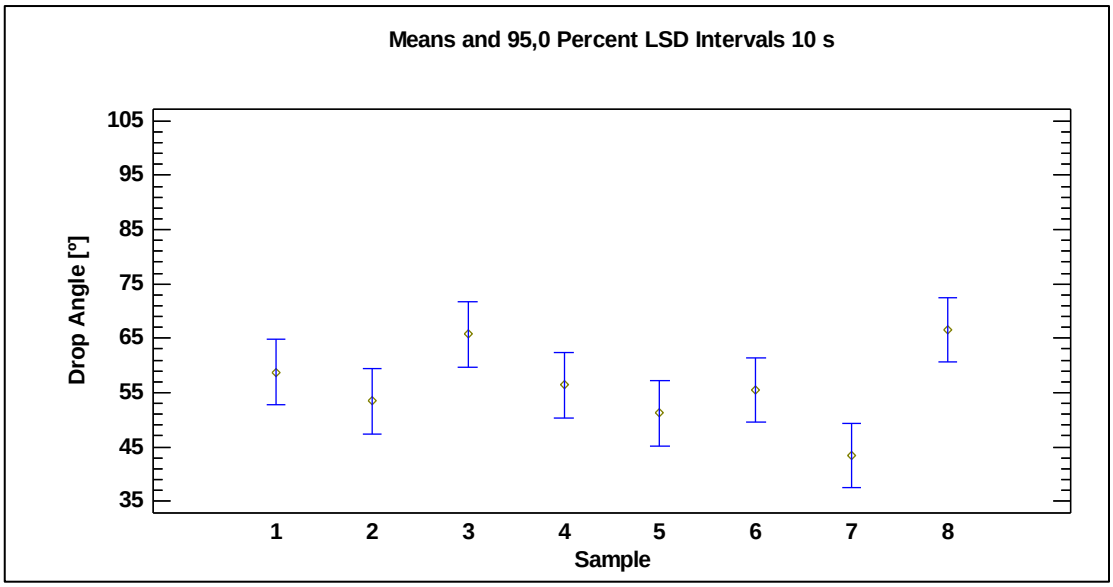


Fig. 5, 6 and 7: statistical graphs for drop contact angle at 0.1, 1 and 10 s from drop application.

In the same way, the obtained statistical data for the adhesion strength are shown below:

Table 3: Statistical results for adhesion strength.

	Adhesion strenght Sample 1 (kgf)	Adhesion strenght Sample 2 (kgf)	Adhesion strenght Sample 3 (kgf)	Adhesion strenght Sample 4 (kgf)	Adhesion strenght Sample 5 (kgf)	Adhesion strenght Sample 6 (kgf)	Adhesion strenght Sample 7 (kgf)	Adhesion strenght Sample 8 (kgf)
Mean:	181	126	165	183	172	202	168	195
Range:	170	70	163	142	176	140	54	170
Standard Deviation:	83	26	61	63	91	70	26	70

The statistical graphs representative of the six specimens for each sample, summarizing all the data collected, can be also shown:

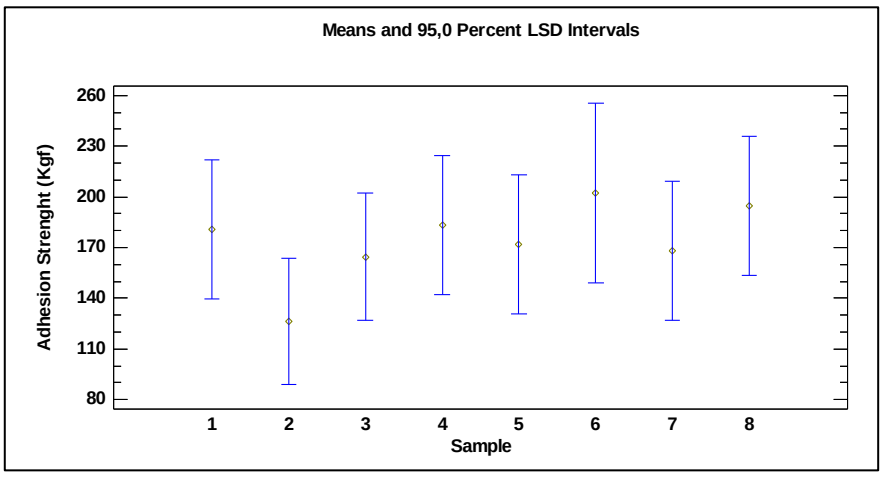


Fig 8: statistical graph for adhesion strength

The results of the average fracture regions are also shown in the following table:

Table 4: Table with the average contributions of the adhesive failure.

Sample	Type of adhesive failure (% of contribution) (nearest 10 %)	
	A (Cohesive)	A / B (Adhesive)
1	0	100
2	5	95
3	8	92
4	16	84
5	22	78
6	20	80
7	76	24
8	28	72

3. RESULTS DISCUSION AND CONCLUSIONS

As it can be seen from Table 2 and Fig. 5, 6 and 7, the obtained statistical results for drop angle show big dispersion, especially at 0.1s and in samples 3, 4, 5 and 8, in which standard deviation value exceeds the 20% of the mean value. Two possible factors can be the reasons of this dispersion: the drop shape is not completely stabilized at early times and the material surface is very heterogeneous (as it can be deduced by the petrography study). The first factor can be reduced by establishing the drop angle comparative study at 10 s (although some samples maintain a high standard deviation at those times). The second factor can't be avoided and it is a general characteristic of any kind of property of natural stone determined in the laboratory.

A multiple sample comparison study can be performed using software for statistics. ANOVA provides a statistical test of whether or not the means of several groups are equal, so ANOVAs are useful for comparing (testing) three or more means (groups or variables) for statistical significance. An ANOVA test between the means of the 8 drop angle variables at the 95.0% confidence level shows that there is a statistical difference between the variables. Repeating the same ANOVA test removing sample 8, the same result comes from the test. If sample 7 is also removed, the ANOVA test shows that the rest of the variables are statistically equivalent at the 95.0% confidence level. Sample 7 and 8 are statistically independent if we perform the ANOVA test for the two variables. Similar conclusions can be extracted from the statistical comparison of angles at 0.1 and 1 s.

These statistical results can lead to the following conclusions, relating to the experimental results obtained in this work:

- The drop angle variable can be considered statistically constant for those samples treated with fine abrasives (from grain 220 to the smaller ones). The mean value of the drop angle at 10 s from drop application considering the six equivalent sets of samples is 56.8º, which means that the surfaces are weattable by water and similar liquids.
- The drop angle variable of samples treated with a coarse abrasive sequence stopping at grain 120 (sample 7) is statistically independent and has a mean value at 10 s of deposition of 43.5º, which means an improvement in the wetting behavior from samples which continue in the polishing line with finer abrasives.
- The drop angle variable of calibrated samples after treated with an abrasive of grain 60 (sample 8) is statistically independent and has a mean value at 10 s of deposition of 66.5º, which means a worse wetting behavior from samples that are further treated with abrasives. If we also show the individual results for each tested specimen, as we do in Fig. 9, we can observe that there are several points in the

sample set in which the drop angle was near to 90º, implying areas with a change in the wetting behavior and an inconvenience for a liquid coating application.

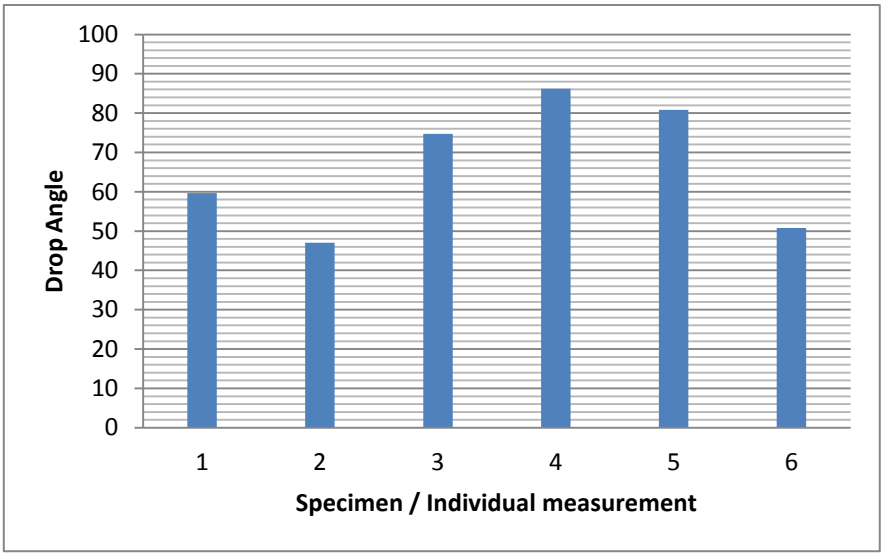


Fig. 9: Individual values for drop angle for Sample 8

Regarding the adhesion strength, again a big dispersion of values is presented, represented by high values of the range and the standard deviation (in samples 1 and 5 the standard deviation value is around the 50% of the mean value). The statistical study of the 8 means obtained via the ANOVA test, shows that there is no significant difference between the means of the experimentally obtained adhesion strengths and that they are statistically equivalent at 95.0% confident level. However, it can be seen an evolution in the behavior of the fracture mechanism from the samples treated with the complete sequences of abrasives including the finest granes to the ones just treated with the coarser granes. Adhesive failure is the complete dominant mechanism in fine grain treated samples, while a mixture of adhesive and cohesive failure occurs on samples at the beginning of the polishing process. Samples treated with coarse abrasives, however, do not continue the trend and this can be due to different surface characteristics, induced by previous calibrating process and that have not been completely removed by the action of just one abrasive. This should have to be studied in the future, as no microscopic characterization of the surfaces has been done in this work.

The main result derived from these facts about adhesion strength and applicable to this case study is that the ideal adhesive state, in which the most predominant adhesive failure is cohesive for the substrate (near to 100%), has not been obtained with the coating systems considered in this experimental work. The best results regarding the type of adhesive failure has been obtained at a point within the polishing sequence, after calibration and the treatment of coarse abrasives (60, 80 and 120).

As a general conclusion, at the view of the partial conclusions showed, it can be said that samples that are calibrated and treated by coarse abrasives (grains 60 and 80) are the most suitable for the coating process with the considered epoxy resin, as they show the lowest contact angles and the highest probability of cohesive failure, implying that the best adhesive conditions are met.

From these results, some activities will be pending for the future to complete the study:

- More detailed study of drop angle and adhesion strength with samples treated with sequences of coarse abrasives (from 60 to 120) and including the study of samples just calibrated.

- Surface topography / profilometry and porosity study of the different surface obtained by the different adhesive sequencies. Reference article [9] can be taken as model for the kind of surface characterization to be performed.
- Study of influence of the liquid characteristics (viscosity and density) of the liquid coating over the final coating adhesive strength. The selected resin for this experimental work was very viscous and it has to be demonstrated if the obtained results can be achievable with other resins.
- Validation of the obtained results with a bigger statistical sample.

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