

DETERMINING THE VALUE OF SURFACE FREE ENERGY ON THE BASIS OF THE CONTACT ANGLE

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ABSTRACT

This paper presents the results of tests concerning the value of surface free energy on the basis of measurements of contact angle with measure liquids: distilled water and diiodomethane. The surface of steel-316L samples was modified in an ozone atmosphere, and the concentration of ozone and the conditioning time of the samples in the reaction chamber were changed. The results of tests concerning the measurements of the value of surface free energy were subject to analysis. Also analysed were the components of SFE: the polar and dispersive components. The obtained test results were analysed in statistical terms. The paper ends with conclusions.

Keywords: energy state, surface layer, contact angle, ozonisation.

INTRODUCTION

The energy state of the surface layer of modern construction materials used in industry is especially important in those technologies in which adhesion is a crucial property conditioning the effects of the process. Such technologies include bonding, the airtight sealing of structures, coating, printing, sintering technologies, and many more [1, 3, 8, 10, 12]. The efficient joining of construction materials requires the correct preparation of the surfaces of bonded elements and the selection of adhesives and sealants with the best properties.

Science and technology know many methods of determining the value of surface free energy (SFE), and brand-new methods are being discovered. For liquids, these are direct methods, and, in the case of solids - indirect methods based mostly on measuring the contact angle of wetting with measure liquids. The following are the most important methods [1, 2, 4, 6, 9, 11, 13, 14] of determining the value of surface free energy: the Fowkes method, the Owens-Wendt method, the van Oss, Chaudhury and Good method, the Zisman method, the Neumann method, the Wu method, etc.

In the light of the current state of the art in basic science, such as physics and chemistry, we know that in interfacial areas, atoms comprising each of the phases are subject to the action of a different force system from the atoms located deep inside the phase. We can distinguish the following phase systems: solid-liquid, solid-gas, and liquid-gas [14]. Atoms located inside a given phase are surrounded by atoms of the same type, and thus are subject to the action of a balanced system of attractive and repulsive forces. However, atoms which are located in the interfacial area or at an interface are subject to a different distribution of forces. On the one hand, they are attracted by neighbouring atoms of their native phase, and, on the other hand, they are also attracted by atoms in the neighbouring phase. Such a system can be defined as an asymmetric field of force. When attractive forces towards one of the phases are strong enough, atoms migrate into this phase as long as the state of balance is reached. Figure 1 demonstrates, in a simplified way, the interactions taking place inside phases with different surfaces in topographic terms, and in their interface.

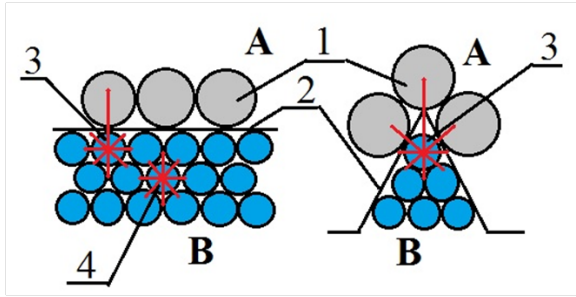


Fig. 1. The impact of surface roughness on intermolecular forces inside the phases, and in the interface: 1 - phase A molecule, 2 - interface, 3 - phase B molecule located in the interface, 4 - phase B molecule located inside this phase

Surface free energy, in qualitative terms, equals the amount of work needed to create a new unit of area, during the division of two balanced phases, in a reversible isothermic process [10]. The measure of surface free energy is [mJ/m²]. On the other hand, surface tension is defined as a force tangent to a given surface, which acts on a unit of length, and the unit is [mN/m]. According to [15, 16], the relation between surface free energy and surface tension is [mJ/m²] = [mN/m]. On the other hand, the author of the paper [10] rightly believes that for solids surface tension is a vector quantity, and the unit of surface free energy is a scalar. Therefore, they cannot be compared directly, although for unary liquids and solids, these are equal values in terms of numbers. The relation between surface free energy and surface tension is (1):

$$\sigma = \gamma + S \frac{\partial \gamma}{\partial S} \quad (1)$$

where: σ - surface tension, γ - surface free energy, S - unit of area of a given body.

For liquids the following relations is assumed (2):

$$\frac{\partial \gamma}{\partial S} = 0 \Rightarrow \sigma = \gamma, \text{ for } S \neq 0 \quad (2)$$

Adhesion energy is a parameter that determines the efficiency of construction-material surface bonding, and is described as the work needed to separate the two phases without interfering with the nature of the interaction, resulting in the creation of a durable bond.

The nature of the interrelation in a solid-liquid-gas system is described by the characteristic Young's equation (3) [10, 15, 16], whose graphical interpretation and the way of measuring the contact angle are presented in Fig. 2.

$$\sigma_{SV} = \sigma_{SL} + \sigma_{LV} \cos \theta_V \quad (3)$$

where: σ_{SV} – surface tension in the solid-gas interface, σ_{SL} – surface tension in the solid-liquid interface, σ_{LV} – surface tension in the liquid-gas interface, θ_V – equilibrium contact angle.

Despite Young's equation having been formulated more than two centuries ago, it is still the basis for the determination of surface free energy of construction materials. Many methods which involve measuring the contact angle of measure liquids are based on this equation.

TEST FACILITY

Tests concerning the measuring of the contact angle were carried out using distilled water and diiodomethane. A measure liquid with a constant density of 4 µl was placed mechanically on a tested surface using a PGX goniometer mechanism.

To geometrically expand the surface and eliminate the physisorption layer, some tested samples were subject to mechanical processing using an orbital sander (a Hilti WFO 280) with a coated abrasive tool with a grit size of P320, over 30 seconds. All samples were cleansed using Loctite 7061 degreaser. Table 1 presents the chemical composition of 316L steel.

After grinding, the subsequent stage of surface preparation (with the appropriate variants) was presented in Table 2.

On the basis of preliminary tests and statistical analysis, the required number of measurement repetitions was estimated.

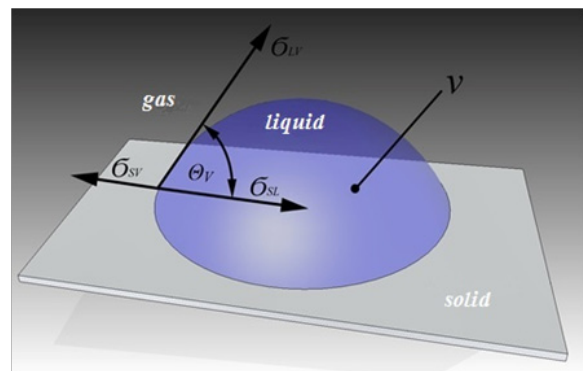


Fig. 2. A graphical interpretation of Young's equation and a model for measuring the contact angle

Table 1. The chemical composition of 316L steel

316L steel									
Element	C	Si	Mn	P	S	Ni	Cr	Mo	N
Value, %	0,011	0,54	1,03	0,040	0,001	10,18	16,71	2,05	0,020

Table 2. The ways of modifying the surface layer

316L steel	
1	Samples before ozonation
2	Samples after ozonation: 20g O ₃ /m ³ in time 10 minutes
3	Samples after ozonation: 20g O ₃ /m ³ in time 30 minutes
4	Samples after ozonation: 50g O ₃ /m ³ in time 30 minutes
5	Samples after ozonation: 50g O ₃ /m ³ in time 45 minutes

Table 3. The preliminary measurements of the contact angle with measure liquids and SFE calculation

316L steel after machining P320			
	Θ _w [°]	Θ _d [°]	[mJ/m ²]
\bar{y}	60.49	29.48	61.68
s	1.2106	0.9864	1.3871
s ²	1.46544	0.97289	1.92400
n	7.50	4.98	9.84

STATISTICAL ANALYSIS

The first stage of testing comprised preliminary tests [5, 7]. After determining the normal distribution of the contact angle values, the required number of measurements of the contact angle was specified on the basis of dispersion analysis and the adopted significance level $\alpha = 0.05$. Before commencing essential tests, a series of preliminary tests were carried out to determine the test size of the contact angle with measure liquids. The number of tests was $n_0 = 10$, and the maximum measurement error was $d = 1^\circ$. The number of measurements was estimated on the basis of contact angle measurements with distilled water and diiodomethane.

Table 3 presents data from the preliminary measurements of the contact angle with measure liquids for 316L steel.

The minimum number of contact angle measurements for distilled water and diiodomethane was determined based on the statistical analysis of preliminary tests. For the analysed construction materials it was assumed that the minimum number of tests should be eight. To increase the accuracy of the measurements, ten reiterations of the measurements were made, and extreme values were discarded.

The preliminary tests concerning the determination of surface free energy aimed at establishing the number of measurements of SFE values (indirect testing by the determination of the contact angle). First, the number of repetitions ($n_0 = 10$) and maximum estimation error ($d = 1 \text{ mJ/m}^2$) were set.

On the basis of the statistical analysis conducted, the minimum number of repetitions was determined in relation to establishing SFE values.

The results of tests were treated as small-size samples. To verify the obtained results the statistics of the Student t test and Fisher–Snedecor F-test were used.

Drawing conclusions on the basis of statistical tests is important in the analysis of data obtained from the tests. The first step in hypothesis verification is testing the variance-equality hypothesis.

Null hypothesis has the form of (4):

$$H_0: \sigma_I^2 = \sigma_{II}^2 \tag{4}$$

Alternative hypothesis (5):

$$H_1: \sigma_{II}^2 < \sigma_I^2 \tag{5}$$

Such hypotheses define a test with one-tailed critical region.

Statistics based on the Fisher–Snedecor distribution was used to verify the hypothesis (6):

$$F = \frac{S_I^2}{S_{II}^2} \tag{6}$$

where: - highest-value variance, - lowest-value variance.

The number of degrees of freedom was determined using the relations (7) and (8):

$$f_1 = n_I - 1 \tag{7}$$

$$f_2 = n_{II} - 1 \tag{8}$$

Using the F coefficient critical value tables, one-tailed critical region is determined (9) and (10):

$$F_{cr} = F_{(\alpha; f_1; f_2)} \tag{9}$$

$$O_{cr} = \langle F_{(\alpha; f_1; f_2)}, +\infty \rangle \tag{10}$$

If it is determined that $F < F_{cr}$, then there are no grounds to reject the null hypothesis, meaning that variances do not differ substantially.

Another stage is the verification of the hypothesis on the equality of the means.

Null hypothesis has the form of (11):

$$H_0: m_1 = m_2 \quad (11)$$

Alternative hypothesis (12):

$$H_1: m_1 > m_2 \text{ or } m_1 < m_2 \quad (12)$$

If the variances are equal, then a test based on the Student's t-distribution is used for verification (13).

$$t = \frac{\bar{y}_1 - \bar{y}_2}{\sqrt{\frac{(n_1 - 1)S_1^2 + (n_2 - 1)S_2^2}{n_1 + n_2 - 2} \left(\frac{1}{n_1} + \frac{1}{n_2}\right)}} \quad (13)$$

If the test of the equality hypothesis demonstrates that variances are different, a test based on the Cochran-Cox adjustment is used (14).

$$c = \frac{\bar{y}_1 - \bar{y}_2}{\sqrt{\frac{S_1^2}{n_1} + \frac{S_2^2}{n_2}}} \quad (14)$$

The number of degrees of freedom was determined using the following relation (15):

$$f = n - 1 \quad (15)$$

Using the $t_{(\alpha;f)}$ coefficient critical-value tables for the Student's t-distribution, the two-tailed critical region is determined (16) and (17):

$$t_{cr} = t_{(\alpha;f)} \quad (16)$$

$$O_{cr} = (-\infty, -t_{(\alpha;f)}) \cup (t_{(\alpha;f)}, +\infty) \quad (17)$$

If it is determined that the $t_{(\alpha;f)}$ statistic value lies within the critical region, then the H_0 hypothesis is rejected for the sake of the H_1 hypothesis.

Unambiguous conclusions can be drawn on the basis of the statistical analysis conducted, with the assumed significance level.

TEST RESULTS

Figure 3 presents the normal distribution chart of the test results of 316L steel following mechanical processing with a coated abrasive tool with a grit size of P320, before ozonisation. The values of surface free energy were analysed. All obtained results of the experiment were subject to normal distribution, which is illustrated in Figure 3.

The normality of distribution was assessed using two tests: the Lilliefors test (Kolmogorov–Smirnov) and the Shapiro–Wilk test. The H_0 hypothesis was adopted based on the analysis conducted.

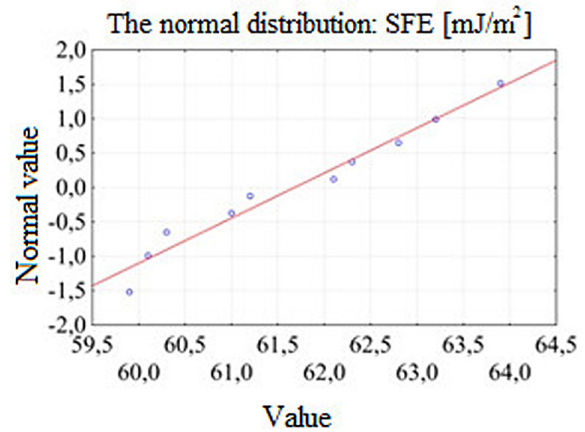


Fig. 3. The normal distribution chart of the test results of surface free energy of 316L steel following mechanical processing

The surface of steel-316L samples was modified in an ozone atmosphere under the following conditions: 1 - samples before ozonisation, 2 - samples after ozonisation: 20 g O_3/m^3 over 10 minutes, 3 - samples after ozonisation: 20 g O_3/m^3 over 30 minutes, 4 - samples after ozonisation: 50g O_3/m^3 over 30 minutes, 5 - samples after ozonisation: 50g O_3/m^3 over 45 minutes.

Figures 4 and 5 show the averaged values of the measure liquid drop volumes. Figure 4 demonstrates the volume of a drop of distilled water, while Figure 5 shows the volume of a drop of diiodomethane, the other measure liquid, based on which the SFE values were established. Despite the measure liquids being placed mechanically by a goniometer mechanism (4 μ l) and their volumes being set, the volume of measure liquid drops actually placed on the surface was subject to volume measurement. The volume of the first measure liquid – distilled water – was at the level of 4 μ l with a standard deviation of approx. 8% in all variants of the surface layer.

The volume of the other measure liquid – diiodomethane – was at the level of 3.5 μ l with a standard deviation of approx. 10% in all variants of the surface layer, despite the initially set volume being 4 μ l. The analysis did not show any correlation between the volume of the sample placed and the technology of the surface preparation.

Figure 6 presents the impact of different methods of surface layer modification of samples made of 316L steel (before mechanical processing) on the value of the contact angle with the measure liquids. Based on the obtained test results, greater diversification in the values of

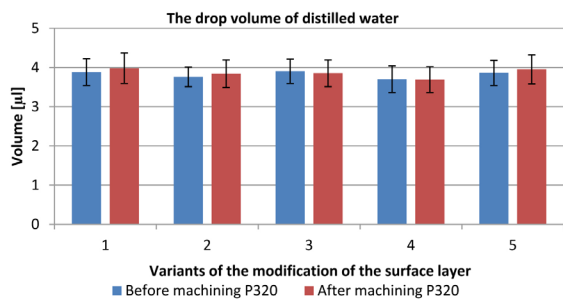


Fig. 4. The volume of a drop of the measure liquid – distilled water

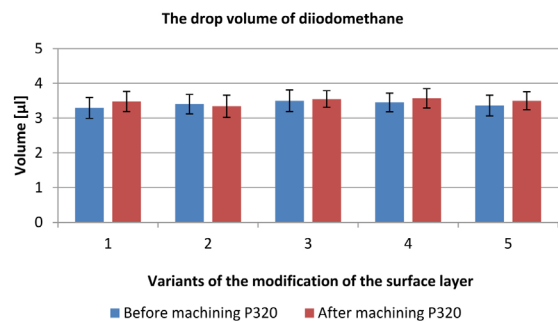


Fig. 5. The volume of a drop of the measure liquid – diiodomethane

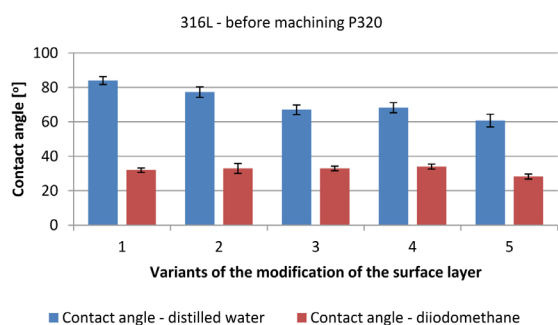


Fig. 6. The impact of surface layer modification on the value of the contact angle before mechanical processing

contact angles with distilled water was observed than in the case of diiodomethane. The values of the contact angle with distilled water were approx. 60° for samples modified in an ozone atmosphere, and up to 84° in the case of samples before ozonisation. The highest decrease in the contact angle with distilled water was observed for the fifth variant of surface layer modification. In comparison with pre-modification samples, the difference equalled 28%. On the other hand, for the contact angle with diiodomethane, the maximum decrease in its value in respect of samples after modification in an ozone atmosphere compared to samples before ozonisation amounted to approx. 11%.

Table 4 juxtaposes photographs of measure liquid drops placed on the sample surfaces before and after the modification of the surface layer in an ozone atmosphere under different conditions.

In the presented photographs one can notice that the measured contact angles with distilled water and diiodomethane decreased as ozone concentration and time of ozonisation increased.

Figure 7 presents the contact angle with measure liquids for 316L-steel samples following mechanical processing with a coated abrasive tool with a grit size of P320, before ozonisation, in relation to the manner of surface layer modification.

In the case of the contact angles with distilled water following mechanical processing, the high-

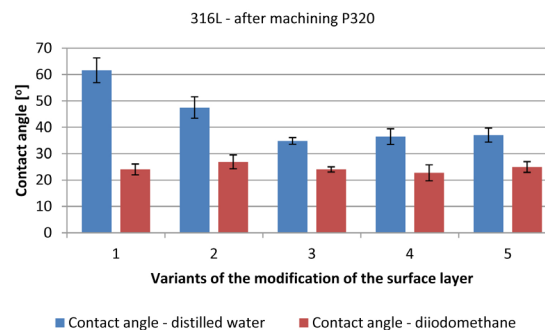


Fig. 7. The impact of surface layer modification on the value of the contact angle after mechanical processing

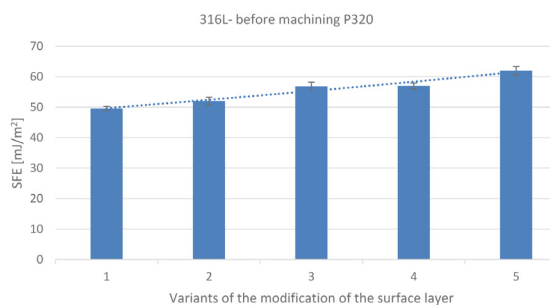


Fig. 8. The impact of surface layer modification on SFE value before mechanical processing

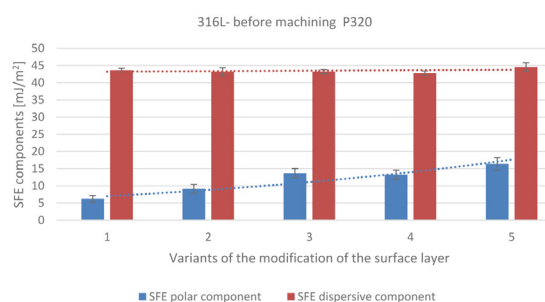





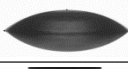
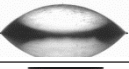
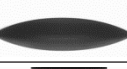





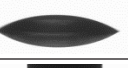
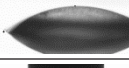






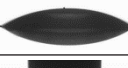
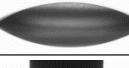






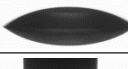
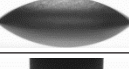
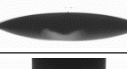




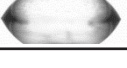
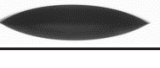
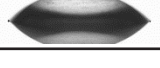
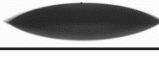


Fig. 9. The share of SFE components depending on the degree of surface layer modification before mechanical processing

Table 4. Photographs of the measure liquid drops used during the measurement of the contact angle

	Before machining P320		After machining P320	
	Distilled water	Diiodomethane	Distilled water	Diiodomethane
1				
				
2				
				
3				
				
4				
				
5				
				

est decrease was observed for the third variant of surface layer modification. In comparison with pre-modification samples, the decrease equalled 43%. On the other hand, for contact angles with diiodomethane, no significant differences were observed. The angle was at the level of 25° with a standard deviation close to 2.5%.

Figure 8 presents the impact of the surface layer modification of samples made of 316L steel (before mechanical processing) on the value of surface free energy. The highest increase in surface free energy was observed in the case of samples corresponding to the last variant, and it amounted to approx. 20% in relation to pre-ozonisation samples. The lowest increase was recorded for the second variant (5%), whereas the maximum value of the standard deviation for the analysed data amounted to 1.84 [mJ/m²].

The highest increase in the SFE polar component for 316L steel before processing (Fig. 9)

amounted to 162% in relation to pre-ozonisation samples, while the lowest increase was 47%. For the analysed data, the maximum value of the standard deviation amounted to 1.84 mJ/m². The SFE dispersive component was at a constant level of approx. 43 mJ/m² with a standard deviation equalling approx. 1 mJ/m².

Based on the tests conducted, an increase in surface free energy was observed in the case of samples after mechanical processing with a coated abrasive tool with a grit size of P320, as a result of the ozonisation process (Fig. 10). The highest increase in surface free energy was observed in the case of samples corresponding to the third variant, and it amounted to approx. 20% in relation to pre-ozonisation samples.

The lowest increase was recorded in the case of the second variant, and it amounted to approx. 10%. For the analysed data, the maximum value of the standard deviation amounted to 1.74 mJ/m².

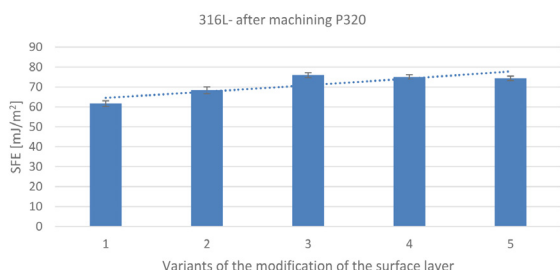


Fig. 10. The impact of surface layer modification on the SFE value after mechanical processing

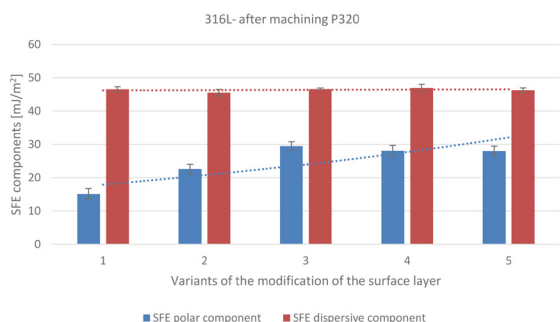


Fig. 11. The share of SFE components depending on the degree of surface layer modification after mechanical processing

Figure 11 presents the impact of the surface layer modification of samples made of 316L steel in an ozone atmosphere (after mechanical processing) on the value of SFE components.

The highest increase in the SFE polar component amounted to 95% in relation to pre-ozonisation samples, while the lowest increase was 50%. For the analysed data, the maximum value of standard deviation amounted to 1.05 mJ/m².

After the tests, the impact of processing with a coated abrasive tool on the value of surface free energy of 316L steel was observed, and a significant increase in this energy was recorded after mechanical processing. This increase amounted

to approx. 20% for pre-ozonisation samples. The polar component of SFE for pre-ozonisation samples, following mechanical processing, increased by 140% in relation to the samples before mechanical processing and ozonisation. It should be highlighted that the value of SFE is a necessary but insufficient condition to obtaining high strength values. The nature of created oxides and their “bonding strength” to the surface are also important.

The analysis of the SFE of steel after mechanical processing revealed that the variance was uniform in all cases; however, the test of the equality of the means indicated significant differences at the adopted significance level $\alpha = 0,05$. The SFE test results are presented in Table 5.

It was found that the process of modifying the surface layer in an ozone atmosphere influences the value of the surface free energy of 316L steel. Also identified was an increase in the value of the surface free energy of 316L steel after ozonisation, in comparison to the pre-ozonisation samples.

Tests and statistical analysis were also conducted for the test results of modifying the surface layer of steel-316L samples before mechanical processing (Table 6). Ozonisation was carried out under the same conditions as in the case of samples after mechanical processing.

The conducted analysis revealed that the variance was uniform in all cases; however, the test of the equality of the means indicated significant differences at the adopted significance level $\alpha = 0,05$. Also in this case ozonisation influences the value of the surface free energy of 316L steel. Also established, in all cases, was an increase in the value of the SFE of 316L steel after ozonisation in comparison to pre-ozonisation samples.

Table 5. The statistical analysis of the SFE test results after mechanical processing

SFE [mJ/m ²]										
					The variance uniformity hypothesis			The means-equality hypothesis		
No.	\bar{y}	S	S ²	Test	Value statistics F	Critical value $F_{(\alpha; f1; f2)}$	Conclusion	Value statistics t	Critical value $t_{(\alpha; n)}$	Conclusion
1	61,68	1,3871	1,9240	-	-	-	-	-	-	-
2	68,36	1,743	3,0380	1-2	1,5790	3,1789	$S_1^2 = S_{II}^2$	-8,996	2,262	$\bar{y}_1 \neq \bar{y}_2$
3	76,06	1,4009	1,9625	1-3	1,020	3,1789	$S_1^2 = S_{II}^2$	-21,883	2,262	$\bar{y}_1 \neq \bar{y}_2$
4	74,61	1,1892	1,4142	1-4	1,3605	3,1789	$S_1^2 = S_{II}^2$	-21,231	2,262	$\bar{y}_1 \neq \bar{y}_2$
5	73,85	1,1984	1,4362	1-5	1,3396	3,1789	$S_1^2 = S_{II}^2$	-19,917	2,262	$\bar{y}_1 \neq \bar{y}_2$

Table 6. The statistical analysis of the SFE test results before mechanical processing

SFE [mJ/m ²]										
					The variance uniformity hypothesis			The means-equality hypothesis		
No.	\bar{y}	S	S ²	Test	Value statistics F	Critical value F _(α; f1; f2)	Conclusion	Value statistics t	Critical value t _(α; f)	Conclusion
1	49,87	1,166	1,3596	-	-	-	-	-	-	-
2	52,33	1,842	3,3930	1-2	2,4955	3,1789	S ₁ ² =S _{II} ²	-3,385	2,262	$\bar{y}_1 \neq \bar{y}_2$
3	56,93	1,361	1,8523	1-3	1,3623	3,1789	S ₁ ² =S _{II} ²	-11,818	2,262	$\bar{y}_1 \neq \bar{y}_2$
4	56	1,678	2,8157	1-4	2,0709	3,1789	S ₁ ² =S _{II} ²	-9,000	2,262	$\bar{y}_1 \neq \bar{y}_2$
5	61,49	1,777	3,1577	1-5	2,3225	3,1789	S ₁ ² =S _{II} ²	-16,402	2,262	$\bar{y}_1 \neq \bar{y}_2$

CONCLUSIONS

The following major conclusions can be drawn on the basis of the experimental tests, analyses and results presentation:

Ozonisation, conducted with the correct parameters, can be an effective and eco-friendly method of establishing the energetic properties of the surface layer of 316L steel for bonding purposes.

Ozonisation, due to its specific physicochemical impact on the surface layer of 316L steel, increases the value of the polar component of surface free energy, which positively influences the strength (primarily long-term strength) of structural adhesives bonds.

The effects of ozonisation greatly depend on the process parameters, especially the ozone concentration and the time of ozonisation.

An increase in the value of surface free energy is important from the perspective of research objectives. Clearly, an increase in the value of surface free energy is a necessary, though insufficient, condition of assessing the adhesive properties of the surface layer of analysed materials. It is worth pointing out that the polar component of SFE plays the greatest role in the increase in the total value of SFE.

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