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Toughness of a brittle epoxy resin reinforced with micro cork particles: effect of size, amount and surface treatment

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ABSTRACT

Structural adhesives are increasingly being used for new applications, replacing conventional bonding methods. Epoxy resins are the most common structural adhesives used due to their suitable mechanical, thermal and chemical properties, as well for their low ductility and low toughness. Several researchers, have in the past decades, found it necessary to reverse these properties and find new ways to increase the toughness of these adhesives. There are many processes depicted in the literature on how to increase the toughness of brittle adhesives, the use of rubber particles being one of the most common. The inclusion of particles (nano or micro) is a successful method to improve toughness of structural adhesives. In the present study, natural micro particles of cork are used with the objective of increasing the toughness of a brittle epoxy adhesive. The concept is for the cork particles to act like as a crack stopper leading to more energy absorption. The influence of the cork particle size, amount and the presence of a surface treatment were studied. Cork particles ranging from 38-53 and 125-250 µm were mixed into adhesive Araldite 2020. The amount

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of cork in the adhesive varied between 0.25 to 1% in volume. The toughness of the adhesive was assessed through fracture tests, using three-point bending specimens. A Taguchi design experiments was used to understand the influence of each parameter under study (amount, size and presence of surface treatment) and the interaction between them. With this research it was possible to conclude that cork can improve toughness and cork amount, size and the use of plasma surface treatment have influence on the mechanical properties.

Keywords: Epoxy, Cork, Fracture toughness, Micro-particles

1 – INTRODUCTION

Due to its versatility, adhesive bonding is one of the most used techniques for joining materials. Adhesives can join a wide range of materials (polymers, ceramics, metals) and the combinations of any of those materials [1,2]. Adhesives have been increasingly expanding their applications in the industry and epoxies are the most common structural adhesive used. Structural epoxies adhesives are mainly used due to their good mechanical, thermal and chemical properties [1]. The epoxy microstructure is very useful for applications in structural engineering, because it presents high modulus of elasticity and strength, low creep, and good thermal strength [2, 3]. Nevertheless, the structure of these thermoset polymers also causes brittleness, with a low resistance to the initiation of cracks and their propagation [4, 5]. Consequently, toughening of epoxies has become a necessity to ensure the suitability of these materials for practical applications. Toughening of these adhesives has been widely studied in the past forty years, and nowadays represents a large field of scientific and technological concern. [4,

6-10]. There are some solutions available to improve toughness of brittle adhesives, like the inclusion of particles (inorganic or organic) [11, 12].

Toughness can be defined as the resistance of the material to fracture when stressed, in other words, the ability of a material to absorb energy and plastically deform without breaking. Toughness is one of the main aspects that govern the strength of materials. Hence, it is important to have full awareness of this property in order to develop a reinforced adhesive [13].

The assessment of toughness of an epoxy reinforced with particles can be made by using fracture tests on bulk adhesive specimens and on adhesive-joint specimens. In these fracture tests, a linear elastic fracture mechanics approach is considered [14]. Bulk tests are a good approach to evaluate the adhesive mechanical properties. These specimens are frequently studied as part of the materials development process.

Nevertheless, since there are some requirements that must be assured, the manufacture of bulk specimens is not an easy task. For instance, the presence of air bubbles must be reduced to obtain a complete filling of the mould and uncontrolled exothermic degradation of the adhesive during cure must be avoided. Furthermore, a uniform distribution of the particles must be assured, in case the adhesive has a second phase (for example a reinforcement material).

The properties of the reinforced adhesive are not only based on the properties of adhesive matrix or reinforcing particles, there are other parameters that contribute to the toughness process, which largely influence the outcome of the composite material. The parameters considered in this research are the volume fraction (amount), size of the particle and the interface particle/matrix; considering always a well-dispersed separate phase in the cured adhesive.

The amount of particles dispersed in a structural adhesive matrix is a very important parameter in the subsequent toughening properties of the adhesive [15-18]. The volume of particles is directly related to the nature of the particles and their mechanical properties, so it is crucial have full knowledge of the particles nature and properties. Typically, for ductile particles, the critical strain energy release rate (G_{Ic}) only raises very slowly with the increased volume fraction and then reaches a plateau value[19, 20]. Particle size is an equally noteworthy parameter and should be evaluated attentively. Some studies[21, 22] indicated that, for adhesives with micro particles, fracture toughness increases with particle size, so some concluded that G_{Ic} decreases with an increase in particle size at lower volume fractions, while critical energy releases G_{Ic} drops with increasing particles size. Nevertheless, this statement is not consensual. Additionally, size is a parameter that influences not just the fracture toughness but also the operative toughening mechanisms in modified adhesives [18, 23-25]. Size is a variable that can be controlled, and its importance is perceived at all stages of the production of toughening adhesive and subsequent application.

The interface between the particles and the adhesive is also a key factor in the toughness process. When this parameter is studied, it is expected that the properties of a composite material, considering a specific surface area, are strongly influenced in the case of smaller particles, since its interface constitutes a much larger area within the bulk material. Hence, a good wetting between adhesive and the particles, favouring a strong bond, should be guaranteed. Consequently, particles will act as crack stoppers and not as defects on the matrix.

Some authors [26] concluded that weakly bonded particles present lower fracture toughness, compared to strongly bonded particles. Furthermore, the bonding strength of the particle/matrix interface is a vital parameter to determine which toughening

mechanism is dominant in the filled system, since strengthening the particle/matrix adhesion increases the efficiency of pinning, but suppresses crack tip blunting. This acts as a crack pinning mechanism, where propagating crack is blocked by rigid particles. However, blunting at the crack tip can also originate through localized shear yielding and the formation of a damage zone due to crack diversion, particle fracture, as well as debonding of the particle/matrix interface [27]. Chemistry of the particle surface is also extremely important, as it defines both the rate of wetting and the strength of interaction with the adhesive. Consequently, to ensure appropriate interfacial interactions, their surface properties must be modified accordingly. Frequently it is suggested that some degree of modification or treatment should be applied to all surfaces prior to adhesive bonding, in order to make the surface more receptive to the adhesive. In this study, plasma treatment was used to modify the surface of the cork particles, since, depending on the selected gases, it can substantially increase the surface wettability and decrease the contact angle. There are several proposed models which acknowledge that plasma treatments, crosslink and reticulate the substrate surface, developing a more active surface and improving wettability due to surface oxidation, introducing reactive groups that increase the surface reactivity. Previous studies observed that the plasma treatment increased the wettability of the cork [28, 29].

In this study micro cork particles were used to increase the toughness of a brittle adhesive. Tests were performed to evaluate the influence of the cork by particle size, amount and the presence of a surface treatment. To better understand the influence of each parameter and the interaction between them, the Taguchi method was used.

2- MATERIALS AND METHODS

2.1 – Materials

Araldite 2020, from Huntsman Advanced Materials (Pamplona, Spain), was the designated adhesive because it is quite brittle, so the improvements on the toughness after the cork particles can easily be perceived. Araldite 2020 is a two component adhesive (100/30 by weight), resin (component A) and hardener (component B). Component A is composed by diglycidyl ether of bisphenol A, (DGEBA) and diglycidyl ether of 1, 4 butanediol (DGEBOH). On the other hand, the component B is composed by isophorone diamine (IPDA).

Cork powder with 38-53 and 125-250 μm size was used. The cork used was supplied by Amorim Cork Composites (Mozelos, Portugal), without any treatment**.**

2.2 – Surface plasma treatment

Plasma treatment was used to modify the surface of the cork particles since it can considerably increase the surface wettability and decrease the contact angle [30]. Low pressure plasma treatment was performed on a Plasma Cleaner chamber from Harrick Plasma (Ithaca, NY, USA), using air as the gas to produce the plasma on a surface of 70.85 cm^2, at 0.29atm of pressure. For the treatment in the chamber, 30 W of electric power for 1 minute was used.

2.3 – Manufacture of bulk specimens

The cork was initially mixed with the resin using a centrifuge mixing machine, SpeedMixer DAC 150™ (Hauschild, Hamm, Germany), for 90 seconds at 1500 rpm.

Before, the cork was mixed with the resin and after that the hardener was added to the mixture. This procedure was the same for the different amounts and cork size. To ensure a better particle distribution after the mixing, the composite was heated to 50°C for 15 minutes, to increase the adhesive viscosity. Afterwards, the composite was mixed again in the centrifuge mixing machine. This procedure was considered the most simple and effective way to prevent agglomeration of cork particles [31].

After, the mixture was cast in a pre-heated steel mould. Release agent was applied to the mould to ensure an easy release of the bulk specimen. A silicone rubber frame was used to apply a hydrostatic pressure to the adhesive, which was hot pressed (2 MPa) for 15 minutes at 100°C (according to the manufacturer's recommendation cure). Specimens were machined from the plates manufactured with a mould [32]. The specimen production plan, varying cork presence, amount, size of cork particles and the presence of surface treatments, is shown in Figure 1.

(Figure 1 near here)

2.4 – Tensile tests

Tensile tests were performed to determine the value of Young's modulus for each of the proposed conditions. For tensile tests, dog-bone specimens with 2 mm of thickness were used [33]. The tensile tests were carried out in an Instron 3367 universal testing machine (Norwood, USA), with a capacity of 30 kN. This test was made at room temperature and at a test speed of 1 mm/min. Three specimens were tested for each condition.

2.5 – Fracture tests on bulk specimens- single edge notched bend

Fracture tests could be performed on bulk adhesive and/or adhesive joints. However, when bulk specimens are used, a more accurate determination of the adhesive properties is achieved. The cured plates were machined to single edge notched bend (SENB) specimens, using standard techniques developed for polymers (ISO 2000) [34]. SENB specimens were used to determine the toughness of the epoxy in terms of the critical-stress-intensity factor, K_{1c}, and the critical strain energy release rate, G_{1c}, satisfying the requirements of ASTM D5045-99 and ASTM E 399 [35, 36]. SENB geometry consists of a centre-notched beam loaded in three-point bending (see Figure 2). The pre-crack (a) was obtained by lightly tapping a razor blade (0.3 mm) into the tip of the machined crack. It is crucial to perform a very sharp pre-crack and eliminate residual stresses around the crack tip, in order to obtain a precise K_{Ic} and G_{Ic} value. The pre-crack length (a) ranged from about 5.4 to 6.6 mm. After opening the pre-crack, it was necessary to measure it with the greatest possible accuracy. For this purpose, a magnifying glass (Zeiss/Germany) was used in conjunction with an image capture software, Leica LAS 4.3 (Leica Microsystems/Germany).

The plane-strain fracture toughness tests were carried out in an Instron 3367 universal testing machine (Norwood, USA), with a capacity of 30 kN. This test was performed at room temperature with a crosshead speed of 10 mm/min, which was fast enough to avoid the viscoelastic behaviour of the epoxy [35]. Five specimens were tested for each condition. Figure 2 shows the geometry of SENB specimens used in this study.

(Figure 2 near here)

The K_Q values were determined using the following equations [35]:

$$K_Q = \left(\frac{P_Q}{BW^{1/2}}\right) f(x) \qquad \text{(Equation 1)}$$

$$(0 < x < 1)$$

$$f(x) = 6x^{1/2} \frac{[1.99 - x(1-x)(2.15 - 3.93x + 2.7x^2)]}{(1+2x)(1-x)^{3/2}} \qquad \text{(Equation 2)}$$

$$x = a/W \qquad \text{(Equation 3)}$$

Where K_Q is a provisional fracture toughness (MPa.m$^{1/2}$), f the shape factor, P_Q is the maximum load (kN), B the specimen thickness (cm), W width (cm), a the crack length (cm). According to standard ASTM D 5045 it is necessary to check the validity of K_Q via the size criteria. It was calculated $2.5(K_Q/\sigma_y)^2$ where σ_y is the yield stress. If this quantity is less than the specimen thickness, B, the crack length, a, and the ligament (W-a), K_Q is equal to K_Q to K_{IC}. Otherwise the test is not a valid K_{IC} test. The G_{Ic} values were determined using the following equation [35]:

$$G_{Ic} = \frac{(1-\nu^2)}{E} {K_Q}^2 \qquad \text{(Equation 4)}$$

Where G_{Ic} is the toughness parameter based on energy required to fracture (kJ/m^2) and ν is the Poisson coefficient.

Standard geometry is recommended over other configurations because these have predominantly bending stress states which allow smaller specimens sizes to achieve plane strain. So, in order for a result to be considered valid, the following criteria must be satisfied:

$$B, a, (W - a) > 2.5\left(K_Q/\sigma_y\right)^2 \text{ (Equation 5)}$$

2.6 – Scanning electron microscopy analysis (SEM)

Scanning electron microscope (SEM) analyses were performed in a JEOL JSM 6301F/ Oxford INCA Energy 350/Gatan Alto 2500 microscope (Tokyo, Japan) at CEMUP (University of Porto, Portugal). This equipment was used to analyse the cork particles, particle distribution and surface fractures. Samples were coated with an Au/Pd thin film, by sputtering, using the SPI Module Sputter Coater equipment, for 120 sec and with a 15mA current.

2.7 – Particle size analysis

Particles size analysis was accomplished using a Malvern Mastersizer 2000 (Malvern, United Kingdom). This equipment was used to evaluate the cork particle size distribution. This technique was used to complement the results obtained in SEM. Three tests were made for each condition.

2.8 – Taguchi design experiments

The Taguchi method was the methodology used to design the experiments [37]. For the selection and definition of a Taguchi experimental plan, seven crucial steps must be considered:

1. Identification of system factors and response;
2. Selection of the levels of the factors to experiment;
3. Selection of the appropriate Taguchi orthogonal array;
4. Assignment of factors and/or interactions to the columns of the orthogonal array;
5. Conducting the tests;

6. Data analysis: average response graphs, ANOVA (analysis of variance)
7. Performing confirmation tests [38, 39]

The Taguchi orthogonal array used contains three variables, corresponding to the size, amount and surface plasma treatment, therefore, a $L_8(2^7)$ it was applied (Table 1). The $L_8(2^7)$ allows to quantify the main effects and interactions between the variables considered. The influence of each variable and its interactions was assessed by the average response and the analysis of variance, ANOVA (SuperANOVA version v1.11, Abacus Concepts, Inc. 1991).

3 -RESULTS AND DISCUSSION

3.1 - Cork particles characterization

The cork particles size, shape and wall thickness were analysed in SEM, for particles with and without plasma surface treatment. In both cases, particles with 125-250 μm size presented a honeycomb structure composed by several cells, some open (edges of particles), but also closed cells (particle core) (see Figures 3 and 4). Particles with 38-53 μm size have damaged cell walls, and in some cases these particles present only cell walls fragments (see Figures 5 and 6). When analysing the surfaces that have been treated with plasma, some differences are observed compared to the particles that were not treated. The thickness of the cell walls of the treated particles is smaller than that of the particles that did not have surface treatment. Measurements were performed at various cell walls and a decrease of cell wall thickness of 3.6% was observed in particles sized between 38-53 μm and a decrease of 3.3% in particles sized between

125-250 µm. These results suggest that the plasma treatment is responsible for the erosion of the cell walls.

(Figure 3 and 4 near here)

(Figure 5 and 6 near here)

3.2 – Tensile tests

In previous studies it was observed that the presence of cork particles (different size and amount) changes the mechanical properties of the adhesive [31]. In order to evaluate the Young's modulus, tensile tests were performed. Analysing Figure 7 it can be clearly observed that the Young's modulus varies with the size, amount and surface treatment of cork particles and is an important parameter to evaluate the toughness of an adhesive, used to calculate the value of G_{Ic}.

(Figure 7 near here)

3.3 –Fracture tests on bulk specimens

Three-point bending tests were conducted to evaluate the mode I critical strain energy release rate (G_{Ic}) of the neat resin and epoxy reinforced with micro particle of cork. Analysing the data represented in Figure 8, it is observed that the amount, size and surface treatment influence the adhesive toughness. Specimens with cork which have surface treatments feature G_{Ic} values lower than those presented by the neat resin. And also, for the same amount of cork, specimens with surface plasma treatment present lower G_{Ic} values. On the other hand, the samples with cork which were not subjected to

surface treatment show higher values of G_{Ic} compared to that of the neat resin. Specimens with 1% of cork present the highest increase compared to the neat resin: 191% and 241% for specimens with 125-250 and 38-53 µm, respectively. Specimens with 0.25% do not show a significant increase as compared with 1% amount, compared to neat resin the increase is more moderate: 103% and 129% for specimens of 125-250 and 38-53 µm, respectively.

(Figure 8 near here)

3.4 –Fracture surface analysis

In order to have a complete grasp of the effect of the particle amount, size and surface treatment on fracture mechanisms, fractographic studies of the SENB specimens fracture surface were carried out, using SEM. This analysis of the fracture surface can be very useful in order to understand the mechanical phenomena occurring during fracture. As previously discussed, the amount, size and surface treatment are responsible for different mechanical properties. Figure 9 and Figure 10 show fracture surfaces with different cork amounts and size for specimens without and with plasma surface treatment, respectively. In both figures, it is evident that micro cork particles are well spread and randomly distributed in the epoxy matrix, and that the fracture surface shows a brittle behaviour. In Figure 7 the fractures surfaces present a quite smooth fracture surface in the slow growth zone. Outside this area, there are spaced “rib” markings perpendicular to the direction of crack growth, in the crack speeding zones, being more evident in specimens with 1% amount 38-53 µm size. It is possible to observe that the major influence on the fracture surface derives from the particle amount. Specimens

with 1% of cork present a less brittle surface, comparing to specimens with 0.25% of cork. Regarding the particles size, it is possible to conclude that specimens with smaller particles, present a less brittle behaviour than specimens with bigger particles. These results are in agreement with the results presented in Figure 9.

Figure 9 near here

Figure 10 shows that specimens with plasma surface treatment have a more brittle fracture surface than specimens without plasma surface treatment. All the fractures display one slow crack at the beginning of the crack growth and one fast crack growth zone when the instability criterion for crack growth is met with the increasing load.

(Figure 10 near here)

3.5 –Analysis of G_{IC} results - analysis of variance and average response

Despite the findings presented in the previous section, it is still difficult to trace a pattern behaviour between the size and amount of incorporated cork and plasma surface treatment. Thus, using a Taguchi orthogonal array (Table 1) is a great tool to analyse trends and observe which variable has the greatest influence and interactions between the given possibilities. In this table p-value is the value for $\alpha < 0.05$ of significance and P is the contribution. Table 2 presents the ANOVA of the data with 95% confidence, and it is easily observed that surface treatment demonstrates the major influence on the fracture toughness results (45.1% of contribution), followed by the amount (16.9%); size is the parameter with less influence (1.1%), is not significant for 95% of

confidence. Analysing Table 2, it is also possible to observe the interaction between the chosen parameters, coming to the conclusion that the strongest interaction is amount vs surface treatment, with 12.7% of contribution.

According to the analysis, surface treatment presents the highest influence on the fracture toughness results (45%). Figure 11represents the main effect of surface treatment. Specimens with plasma surface treatment present a lower value of G_{Ic}, on the other hand, specimens without surface treatment present higher G_{Ic} values but also a higher dispersion of the results. As this study is aimed to achieve the best combination to improve the toughness of the adhesive, it can be concluded that the surface treatment will not be the best option. While the surface treatment improves the properties of wettability between the adhesive and cork particles, the cork particles mechanical properties and structural integrity are compromised.

(Figure 11 near here)

Figure 12 represents the effect of particle amount on fracture toughness. It is observed that specimens with 1% of cork show higher values of G_{Ic}, although presenting larger dispersion. Cork particles do not have a standardized geometry; its structure may vary depending on biological and mechanical factors, which are extremely difficult to control. So there is an inherent dispersion of results that stems from the conditions of the cork particles. With the increase of the amount of cork particles, the results dispersion also increases, as seen in Figure 12. As mentioned in Table 3, the cork particles amount represents an influence of 16.9% on G_{Ic} results. This result can also be

observed by the line slope which joins the two graphed values. The lower the influence of a parameter, the lower the slope of the line.

(Figure 12 near here)

Figure 13 shows the effect of size on fracture toughness. The fracture toughness of specimens reinforced with small particles, presents higher values compared to specimens reinforced with larger particles. Although, the scatter in both cases is significant, it is equally difficult to draw meaningful conclusions regarding this parameter. For 95% of confidence is not significant, as already verify with ANOVA.

(Figure 13 near here)

Figure 14-16 present the interactions between the three parameters: amount, size and surface treatment. It is important to study the influence of each parameter, but also the interaction between parameters to better optimize the process in order to select the best combination possible. Figure 14 presents the interaction between particle amount and surface treatment. This interaction represents a contribution of 12.7% on total variation, indicating a high interaction. With plasma surface treatment there are no significant fluctuations with varying particle amounts, but without plasma treatment it is clear that specimens with 1% of cork particles show a higher G_{Ic}, comparing to 0.25% of cork.

(Figure 14 near here)

Figure 15 presents the interaction between surface treatment and particle size, which represents a contribution of 0.7 %. Similarly, when comparing the interaction between

surface treatment and particle amount versus the interaction between surface treatment and particle size, surface treatment is shown to exert an important influence. Specimens with plasma surface treatment present low toughness values, regardless of particle size. Inversely, the behaviour of specimens without plasma surface treatment differs with particle size, as specimens with small particles present higher values of G_{Ic}. However, it must be noted that there is significant dispersion in these results and therefore this can only be considered as a trend.

(Figure 15 near here)

Figure 16 shows the interaction between size and amount of cork particles, which represents the lowest contribution (-0.5%). In a first analysis, small particle amounts show lower values than higher amounts, regardless of size. However, the dispersion in both cases is significant, not being possible to draw firm conclusions concerning this interaction.

(Figure 16 near here)

3.6 –Taguchi analysis of G_{Ic} results - multiple regression

A multiple regression can be used to obtain a G_{Ic} prediction, constructed using the relationship between the three independent variables. The regression coefficients of G_{Ic} values versus the three independent variables are given in *Table 3*.

With these data points it is possible to formulate an equation that allows to predict the mechanical behaviour of the adhesive by altering the size, amount and the application of

plasma surface treatment of micro cork particles (see Equation 6). In this equation, surface treatment is a dummy variable, taking the value "0" for specimens without plasma surface treatment and "1" for specimens with plasma surface treatment. This equation is valid for particle size between 38-250 µm and amount between 0.25 and 1%, with a determination coefficient (R^2) of 0.65.

$$G_{Ic} = 0.80674 + 0.39272 \times Amount - 0.00065 \times size - 0.47557 \times surface\ treatment \quad \textit{(Equation 6)}$$

The experimental results were used to validate the formulated equation. In addition to the previous tested conditions, three additional conditions that have not been used for the formulation of the equation were tested: neat resin, specimens with 0.5% 125-250 size without surface treatment and specimens with 1.5% 125-250 size without surface treatment. The values presented by the specimen neat resin and 1.5% 125-250 size without surface treatment are not covered by *Equation 6*, being outside of its range of values. However, this analysis was made to observe if the values of the equation can be extrapolated. Figure 17 presents the experimental values and also the analytical values obtained by Equation 6. Analysing the data, it was found that the correlation between the experimental values and the analytical values is not always perfect. However, the equation proves to be a useful tool to predict the mechanical behaviour of the composite material, as it provides a reasonable estimate of the experimental value. Moreover, as observed for the results of the samples of 1.5% and 125-250 particle size without surface treatment, it is not advisable to extrapolate the results to values outside the range of variables considered, since the prediction may not be precise.

(Figure 17 near here)

4 – CONCLUSIONS

The effect of particle size, amount and surface plasma treatment of micro cork particles on the fracture toughness of a brittle epoxy resin was evaluated through tensile tests and bulk fracture tests, and later analysed using the Taguchi method. These tests were performed on neat epoxy resin and epoxy resin reinforced with cork particles. The following conclusions can be drawn:

- Plasma treatment is responsible for an erosion of cell walls, leading to a decrease in cell wall thickness;
- Young's modulus varies with the size, amount and plasma surface treatment of cork particles and is an important parameter to evaluate the toughness of an adhesive used to calculate the value of G_{1c};
- The particle amount, size and plasma surface treatment have an influence on the adhesive toughness. Specimens reinforced with cork particles which were subjected to surface treatments feature G_{Ic} values lower than those of the neat resin. In contrast, the specimens with cork without surface treatment show higher values of G_{Ic} compared to those of the neat resin;
- Fracture surfaces are in agreement with the G_{Ic} values: higher values of G_{Ic} are consistent with less brittle fracture surfaces;
- The Taguchi method is a practical tool to analyse parameters and observe variable influences and their interactions. Surface treatment shows the main influence on the G_{IC} results, followed by the particle amount; particle size is the

parameter with less influence. Regarding the interaction between the parameters, the strongest interaction is amount vs surface treatment;

- The formulated equation is shown to be an expedited tool for predicting G_{IC} results.

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Table 1 - Taguchi $L_8(2^7)$ orthogonal array, with all variables studied (size, amount and plasma surface treatment).

Test	**Variable**		
	Size µm	**Amount %**	**Plasma surface treatment**
1	53-38	0.25	with
2	53-38	0.25	without
3	53-38	1	with
4	53-38	1	without
5	125-250	0.25	with
6	125-250	0.25	without
7	125-250	1	with
8	125-250	1	without

Table 2 - ANOVA analysis with all parameter and interactions, considering G_{Ic}.

Source	*df*	*Sum of squares*	*Mean square*	*F-value*	*P-value*	*P (%)*
Amount (%)	1	0.86752	0.86752	28.38559	0.001	16.9
Size (µm)	1	0.08429	0.08429	2.75810	0.1062	1.1
Surface treatment	1	2.26170	2.26170	74.00320	0.0001	45.1
Amount (%) vs size (µm)	1	0.00451	0.00451	0.14753	0.7034	-0.5
Amount (%) vs surface treatment	1	0.65709	0.65709	21.50007	0.0001	12.7
Size (µm) vs surface treatment	1	0.06757	0.06757	2.21097	0.1465	0.7
Residual	33	1.00855	0.03056			24.1
total	39	4.951230				100

Table 3 - Regression coefficients of G_{Ic} values versus 3 Independents, with R^2 of 0.65

	Coefficient	*Std. error*	*Std. Coefficient*	*t-Value*	*P-value*
Intercept	0.80674	0.09495	0.80674	8.49690	<0.0001
Amount (%)	0.39272	0.09264	0.41859	4.23938	0.0001
Size (µm)	-0.00065	0.00049	-0.13048	-1.32147	0.1947
Surface treatment	-0.47557	0.06948	-0.67587	-6.84508	<0.0001