Influence of the size and amount of cork particles on the toughness of a structural adhesive

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ABSTRACT

The inclusion of particles (nano or micro) is a method to improve the mechanical properties such as toughness of structural adhesives. Structural adhesives are known for their high strength and stiffness but also for their low ductility and toughness. There are many processes described in the literature to increase the toughness, being one of the most common the use of rubber particles. In the present study, natural micro particles of cork are used with the objective to increase the toughness of a brittle epoxy adhesive. The idea is for the cork particles to act like as a crack stopper leading to more energy absorption. The influence of the cork particle size and amount were studied. Particles of cork ranging from 38 to 250 μm were mixed in the epoxy adhesive Araldite 2020 from Huntsman. The amount of cork in the adhesive was varied between 1 and 5% in weight. Surface treatment (low pressure plasma) was applied to the cork powder to assess the effect of the interaction adhesive-cork with several degrees of adhesion.

Keywords: Adhesive, Cork, Surface treatment, Impact toughness

INTRODUCTION

Structural adhesives are often the best solution to join two components, in relation to traditional solutions, such as welding for example. One of the most common structural adhesive is the epoxy resin. The densely cross-linked molecular structure of structural adhesives is responsible for the good properties of these materials, but unfortunately it also makes them inherently brittle with poor resistance to crack initiation and propagation [1,2]. Structural adhesives are known for their high strength and stiffness but also for their low ductility and toughness. The ability of an adhesive to absorb energy without catastrophic failure can be increased through toughening of adhesives with a second phase. This results in enhanced resistance to fracture with minimal change in the gross properties of the matrix resin [3]. The inclusion of particles (nano or micro) is a method to improve the mechanical properties such as toughness of structural adhesives [1]. There are many processes described in the literature to increase the toughness, being one of the most common the use of rubber particles [4]. However, natural materials are gaining attention as reinforcements of polymeric matrices due the thermal properties, low density, low cost and sustainability of the raw material [5]. Cork is a biological material with unique properties, produced by the cork oak. *Quercus suber L.* is the botanical name for a slow growing, evergreen oak that flourishes only in specific regions of the Western Mediterranean (Portugal, Spain, Southern France, part of Italy and North Africa) [4-6]. Portugal is the leadership of the world market relatively to this raw material, producing three-quarter of the total production. Cork may be described as a homogeneous tissue of thin-walled cells, regularly arranged without intercellular space. Cork has reveals an alveolar structure, similar to a honeycomb, without empty spaces between contiguous cells, which are therefore closed units [9].

These structural properties could be very useful to reinforce brittle resins, especially to improve the toughness as the closed cells could work to absorb the impact. However, the properties of a resin/cork composite are not only dependent of the materials properties, but also on their interfacial adhesion properties between the cork and the resin, size and amount of cork particles and mixing conditions [5]. Cork is hydrophobic due the suberin (main component of cork composition) and this fact could deteriorate the adhesion between cork particles and the epoxy resin. The hydrophobic properties could be altered using surface modification. There are several surface treatments to improve the cork-matrix adhesion with a positive effect on the mechanical properties of the composites [5]. Plasma treatment is one of the most versatile techniques in surface modification. Atmospheric pressure plasma is useful to activate the surface and improve the adhesion. This activation consists in grafting chemical functionalities on the surface in order to increase its surface energy. The plasma composition has influence on the treated material properties [10].

The cork particles should create obstacles to the propagation of the cracks thus increasing the toughness of the adhesive. Besides being apparently technically possible, this technique would also allow the use of this product (cork powder), which is not exploited by the cork industry that has an important impact in the Portuguese economy. Cork powder is generally burnt leading to unnecessary energy consumption and frequent accidents. The use of this material would give a new application perspective to the cork industry with potential benefits. Therefore, different amounts of cork and different particles sizes were included in a brittle epoxy to analyse the influence of these particles on the behaviour of cork/resin composite.

EXPERIMENTAL

1 - Materials

Cork powders, without any treatment, with different sizes (38-53 μm and 125-250 μm) were used. This cork powder was supplied by Amorim Cork Composites (Mozelos VFR, Portugal).
The selected adhesive was Araldite 2020, from Hustsman Advanced Materials (Pamplona, Spain). This adhesive is a bicomponent (100/30 by weight), low viscosity (150mPa.s), transparent epoxy adhesive that cures at 100 ºC, during 15 minutes. The Young's modulus of this adhesive is 3100 MPa, its tensile strength is 40.6 MPa and 5.8%.
This material was selected because it has a brittle behaviour, so the improvements on the toughness after the cork particles inclusion are easily seen.

2 – Manufacture of specimens

A homogeneous mixture of the cork powder in the resin must be assured to avoid the introduction of air bubbles and a uniform distribution of particles. The cork was mixed with the resin using a centrifuge mixing machine, SpeedMixer DAC 150™ (Buckinghamshire, UK), during 90 seconds at 1500 rpm. Specimens with and without cork were manufactured, with different surface treatment, different amount and cork particle size.

To assess the dispersion of the cork particles in the resin, thin layers of 5 μm which were cut by a microtome. Cork particles were coloured with methylene blue. A Leika Optic transmission microscope (OTM) was used.

3 - Surface treatments

Plasma treatment was used to modify the cork particles surface, since, depending on the selected gases, it can increase substantially the surface wettability and decrease the contact angle. The atmospheric plasma equipment used was a Plasma Treat GmbH (Steinhagen, Germany), which works in a frequency of 17 kHz and a high tension discharge of 20kV and a rotatory torch (1900 rmp). This system has a platform that allows to control of the treatment velocity automatically. These treatments were made at 8 mm from the surface and at 5m/min, on cork boards of 100x200x3 mm^3. Figure 1 shows a scheme of the cork board used in the tests, with indication of the sections of the cork; radial section is represented by a "A", tangential section by a "B" and axial or transverse section by a "C".

Figure 1- Schematic representation of the cork sections in the cork board.

To measure the wettability of natural and treated cork, a goniometer OCA 15 (DataPhysics, Neurtek Instruments, Eibar-Spain) was used. To measure the contact angle, samples were placed in a chamber, at 25 ºC, satured with water vapour.

4 - Density

The density of treated and untreated cork particles was measured using a helium picnometer micromeritics AccuPyc 1330 de NEURTEK INSTRUMENTS (Spain).

The density of the impact test specimens was measured by Archimedes principle.

5 - Toughness impact test

To evaluate the impact toughness of the composite resin/cork several specimens were made varing the amont of cork, size of particles and surface treatment. Impact Charpy specimens according ASTM E23-02a were manufactured. Figure 2 shows the dimensions of machined specimens.

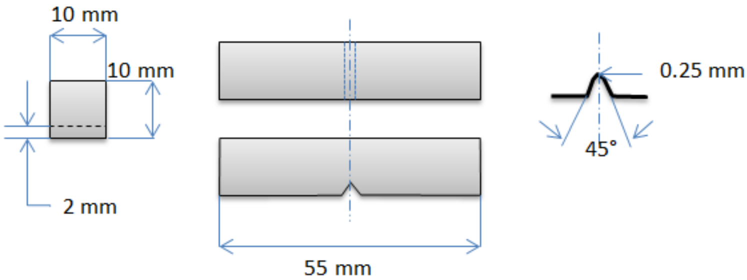


Figure 2- Dimensions of type A Charpy Impact test specimens.

The toughness impact tests were made in a Rosand V1.01 machine. This test was made with a mass of 3.996 kg, at room temperature and with an initial velocity of 1.57 m/s. Three specimens were tested for each condition.

6 - SEM analysis

Scanning electron microscope (SEM) analyses were made in a JEOL JSM 6301F/ Oxford INCA Energy 350 / Gatan Alto 2500 microscope. This equipment was used to analyse cork particles before incorporation in the resin and to analyse the surface fracture of the composite after the impact tests.

RESULTS AND DISCUSSION

1 - Surface properties

Figure 3 and Table 1 show that with atmospheric plasma treatment the contact angle between cork surface and the water drop decreases. Table 1 show that the contact angle between water drop and the various cork surfaces does not vary substantially. This indicates that the adhesion of the cork particles will be uniform through the cork particles surface.

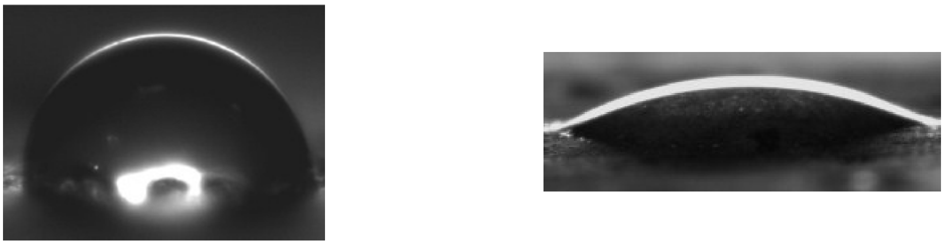


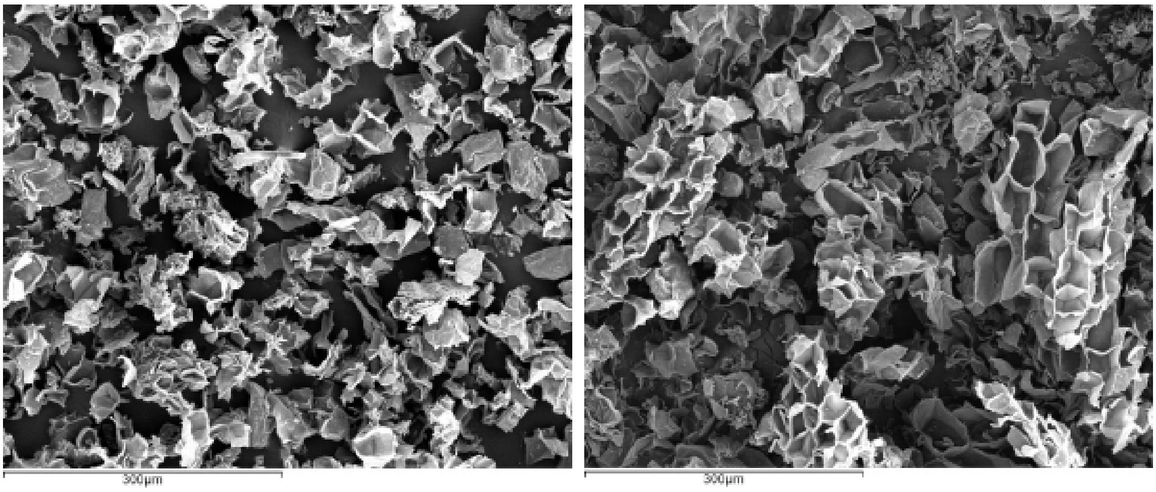
Figure 3- Shape of the water drop in cork surface, without treatment (left) and with atmospheric plasma treatment (right).

Table 1 - Contact angle between water drop and cork surface.

Section	Treated specimen	Untreated Specimen
Radial	30 ± 4	101 ± 11
Tangential	33 ± 7	99 ± 18
Axial	37 ± 2	103 ± 7

2 - SEM cork particles characterization

The cork particles size and shape were analysed in SEM. Figure 4 shows that particles with different sizes have different cell structures. Particles with 38-53 μm have a destroyed honeycomb cell structure, with several cells presenting an open structure and some just a single cell. On the other hand, particles with 125-250 μm size have a honeycomb structure composed by several cells, some open (edges of particles), but a few cells are closed (particle core).



a) b)

Figure 4 - Microstructure of cork powder; a) particles with 38-53 µm size, b) particles with 125-250 µm size.

Cork powder density changes with atmospheric plasma treatment. Figure 5 the shows density of cork particles with different sizes and treatments. The density decreases with plasma treatment. This effect may be because the plasma torch erodes part of cork surface. This increases the surface roughness, but leads to a weight loss.

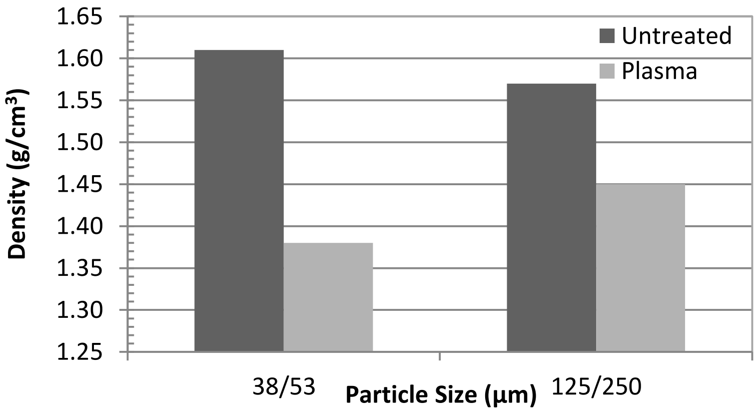


Figure 5- Density of cork particles, with different sizes, untreated and with atmospheric plasma treatment.

3 - Toughness impact properties

Figure 6 shows the variation of the energy absorbed in the impact at load peak and at rupture. Figure 7 shows the displacement of the specimens during the test, in the two considered moments. It is notorious that the presence of cork influence the results. Specimens with 1% of untreated particles with 125-250 µm have a distinctive behaviour. These specimens show a better behaviour compared to the other composite specimens. They absorb more energy at rupture and give a higher displacement.

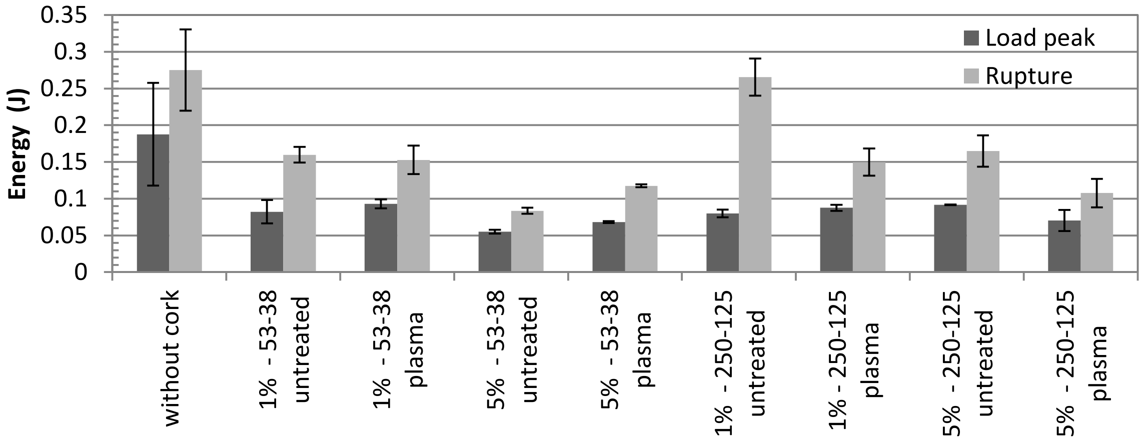


Figure 6 - Energy absorbed in the toughness impact tests, at the load peak and at rupture.

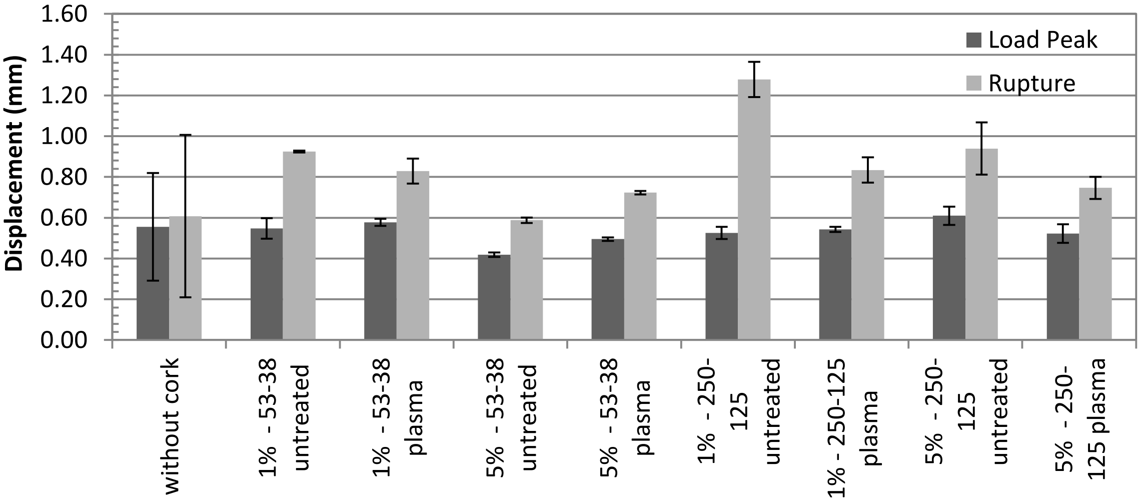


Figure 7 - Displacement of the specimens in the toughness impact tests, at the load peak and at rupture.

Cork has good impact behaviour due to its cell structure disposition, giving a pillow effect. The cells compress, absorbing the impact. But if in the composite the particles do not have an intact cell structure, this effect disappears. Therefore, specimens with small particles are expected to have a worse behaviour than particles with 125-250 µm size. When in contact with resin, cork particles are surrounded by resin but the resin might not penetrate is core. Figure 8 shows images obtained with OTM and it can be seen that the core remains without resin; this was observed for all samples analysed. The behaviour of cork/resin composite is also influenced by the number of cells of the particle.

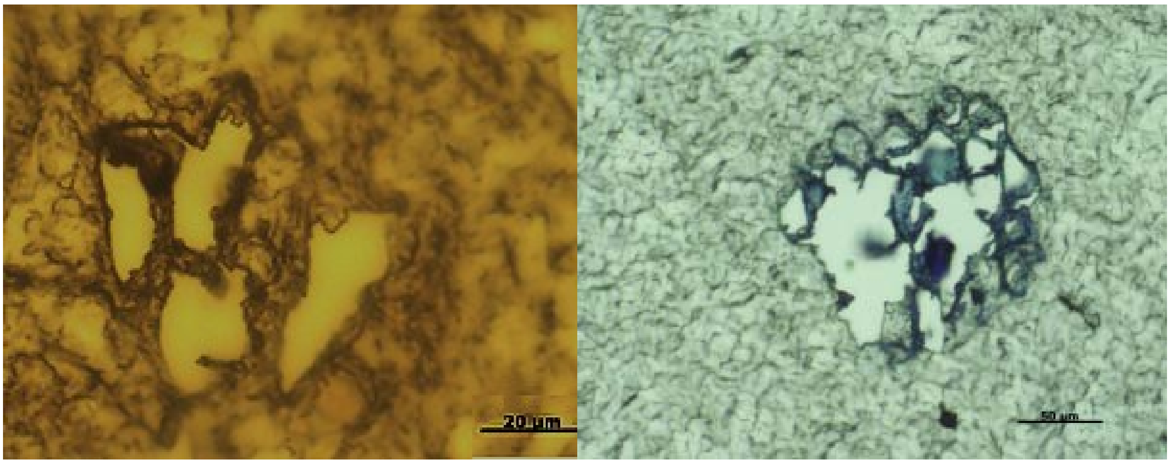


Figure 8 - Resin with cork particles. Left - Closed cell structure. Right - Destroyed cell structure colored with methylene blue.

Figures 6 and 7 show that the plasma treatment gives worse results than untreated cork particles. This treatment improves the contact angle and the wettability, improving the adhesion between cork and resin. However, this treatment at the same time destroys part of the honeycomb structure of the cork cells. In addition, the cork particles damage can facilitate the resin penetration which could decrease the pillow effect of the cork, decreasing the energy absorption. If the resin penetrates inside of the cork cells, the specimen's density should increase, compared to the specimen without cork. However, Figure 9 shows that the density variation is not substantial, considering the associated error. Therefore the interpretation may be regarded with caution.

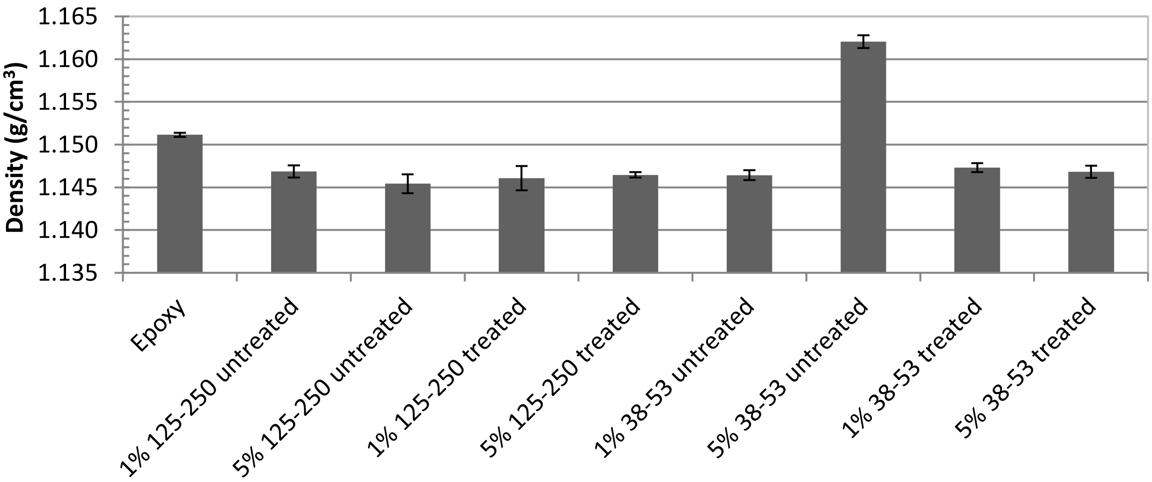


Figure 9 - Density of composite specimens with different surface treatments, amounts and size of cork particles.

Specimens with 1% of cork untreated particles (125-250 µm) presented the best combination of cork amount and particles size. Particles have an undamaged structure and work together with the resin and increasing the energy absorption of the composite.

4 - SEM surface fracture analysis

Figure 10 shows the fracture surface of a specimen without cork and a detail of fracture propagation.

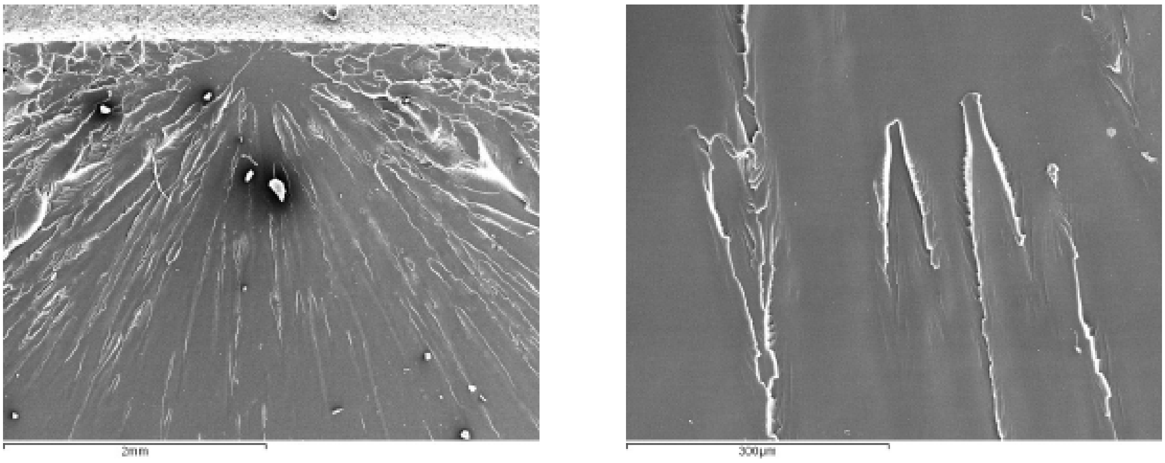


Figure 10 - Fracture Surface of a specimen without cork particles. Left – Overview of fracture surface. Right – Detail of fracture surface.

Figures 11 and 12 show the fracture surface of specimens with 1% of cork particles of size 38-53 µm (treated and untreated respectively). These surfaces have a more brittle behaviour compared to that of the resin without cork because the surface is smother.

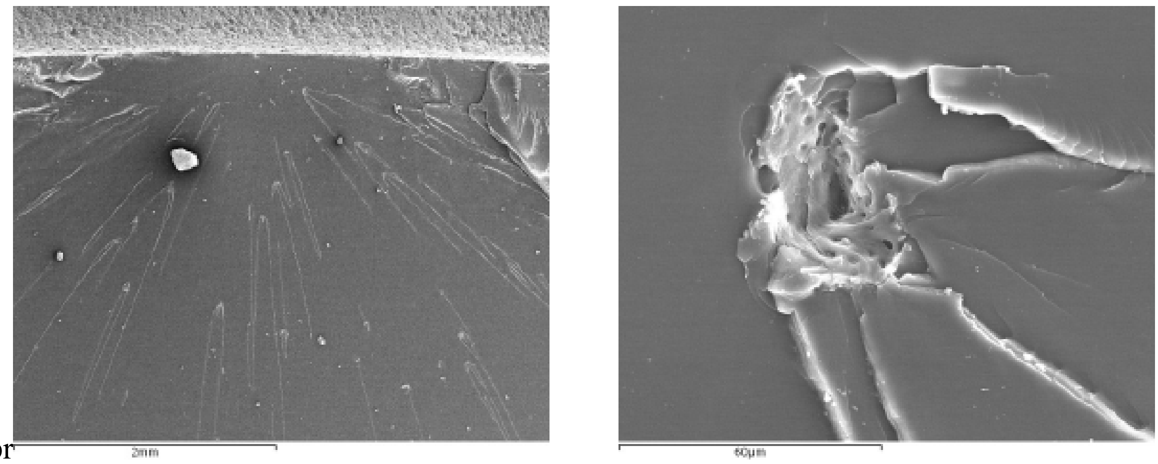


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Figure 11 - Fracture surface of a specimen with 1% of untreated cork (38-53 µm). Left – Overview of fracture surface. Right – Detail of fracture surface.

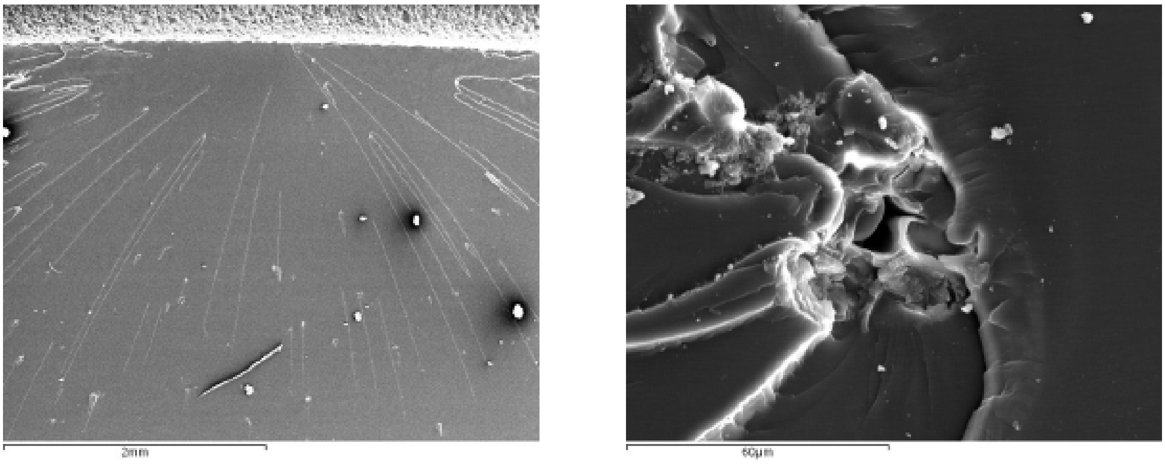

Figure 12 - Fracture surface of a specimen with 1% of treated cork (38-53 µm). Left – Overview of fracture surface. Right – Detail of fracture surface.

Figures 13 and 14 show the fracture surface of specimens with 1% of cork particles with 125-250 µm size (treated and untreated respectively). In both figures, it is notorius that cork particles are empty (no penetration of resin), promoting energy absorption. These figures show that there is several crack planes close to the cork particles which indicates that cork is acting like an obstacle to crack propagation.

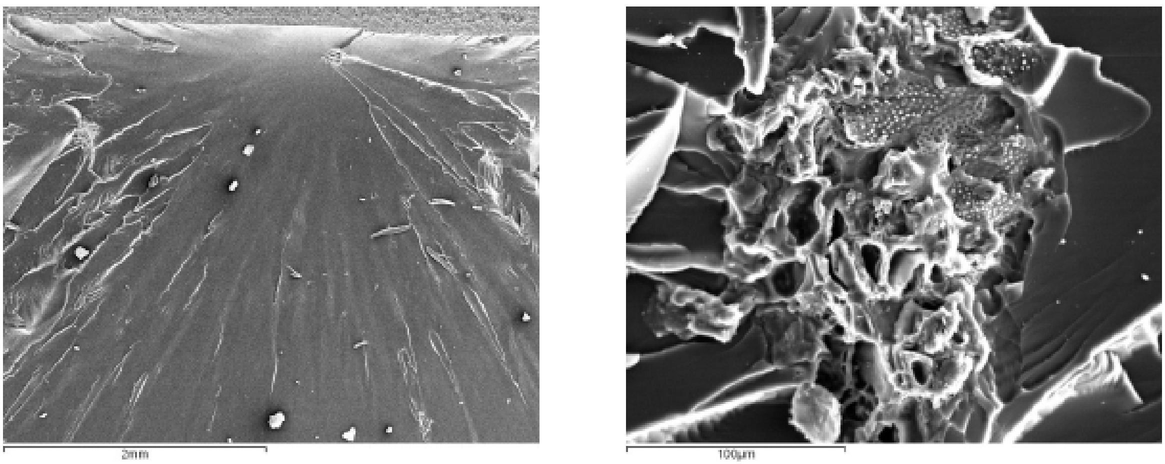

Figure 13 - Fracture Surface of a specimen with 1% of untreated cork (125-250 µm). Left – Overview of fracture surface Right – Detail of fracture surface.

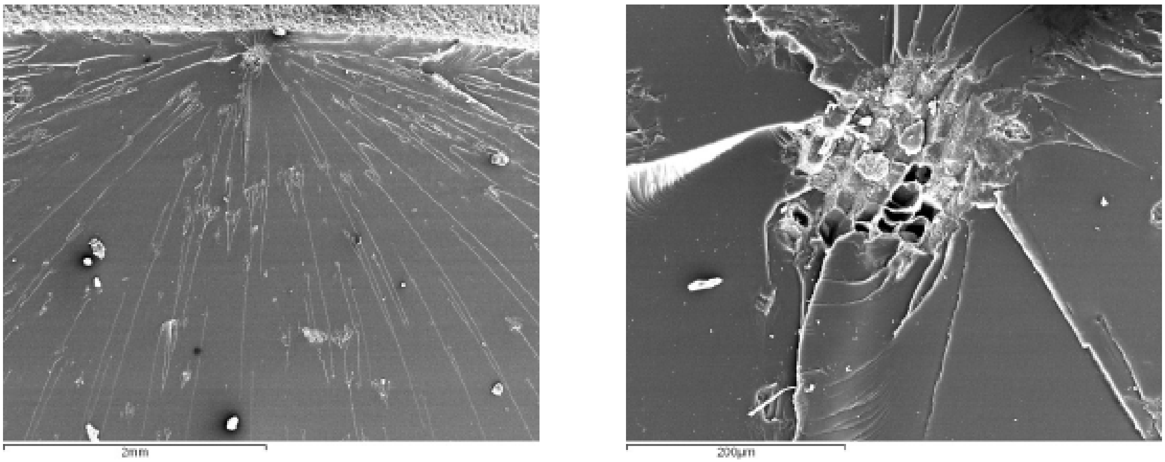

Figure 14 - Fracture Surface of a specimen with 1% of treated cork (125-250 µm). Left – Overview of fracture surface. Right – Detail of fracture surface.

CONCLUSIONS

The influence of the size and amount of cork particles on the toughness of a structural brittle adhesive was evaluated by impact test and surface analyse.The following conclusions can be drawn:

- Atmospheric plasma surface treatment increases the contact angle and wettability of cork. There is an erosion of the surface which increased roughness, promoting adhesion between cork and resin. In cork particles, this surface treatment must be optimized. Cork wall cells are thin and if the treatment time or the distance of the torch are not the best, these walls can be destroyed. In future studies this effect must be analysed.

- SEM and OTM analysis show that most of cells are not filled with resin. The amount of cork, size of particles and surface treatments cause different fracture behaviours.

- Small amounts of cork particles with a structure composed by several cells and with well-preserved wall cells incorporated in a brittle resin present a better impact energy absorption than large amounts or small particles

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