EFFECT OF DIFFERENT SILANE COUPLING AGENTS ON TENSILE AND FLEXURAL PROPERTIES OF BASALT FIBRE-EPOXY COMPOSITES

J. Kano-Ibarretxe[1*], R. Hernandez[1], I. Mondragon[2†]

[1]*Leartiker, Materials dept., Lea Artibai Ikastetxea S. Coop, Markina-Xemein (Spain)*
[2]*Escuela Universitaria Politécnica de San Sebastián, University of the Basque Country, San Sebastián (Spain)*
**jcano@leartik.com*
This paper is dedicated In memoriam of Professor Dr. Iñaki Mondragon Egaña.

Keywords: trialkoxysilane coupling agents, microbond test, compression molding, basalt fibre.

Abstract
The present work aimed to analyze the influence of interphase adhesion level on micro and macro-mechanical behavior of unidirectional basalt fibre epoxy composites. The study was evaluated for as-received, unsized and γ-aminopropyltriethoxysilane, γ-glycidoxypropyltrimethoxysilane and γ- methacryloxypropyltrimethoxysilane sized fibres and their composites. The unsized fibres were obtained by immersion in acetone and its efficiency was evaluated by scanning electron microscopy (SEM). The micromechanical characterization was carried out by means of monofilament tensile test, Weibull two-parameter distribution and microbond test. The macro-mechanical characterization was made by tensile and three-point bending tests. The scatter of the microbond results and the similar tensile and flexural results for as-received and unsized composites, lead to further sizing elimination method efficiency study.

1 Introduction

The high performance properties of fibre reinforced polymeric composites are not simply the sum of the properties of their constituents. The nature of the fibre/matrix interphase plays an important role in determining composites behavior at the required mechanical, thermal and chemical conditions. An efficient load transfer through the interface ensures the effective utilization of the strength and stiffness that the reinforcement can provide to the composite material. It is accepted that weak interfaces give rise to relatively low strength and stiffness but highly tough composites; while strong interfaces lead to high strength and stiffness but brittle composites [1].

Coupling agents, specially trialkoxysilanes, have been extensively used as fibres' surface treatment in order to enhance the interface adhesion between reinforcement and matrix [2,3]. These silane coupling agents should have at least two functional groups which may respectively react with the two phases thereby creating a chemical bonding between them.

Due to the chemical structure of the silane coupling agents that have **(**RnSiX(4-n)), they are suitable to promote the adhesion of inorganic substrates with organic materials, such as polymeric matrices [4]. R is a nonhydrolyzable organic moiety which reacts with the polymer matrix and the X represents alkoxy moieties, most typically methoxies or ethoxies which react with the various forms of hydroxyl groups providing the linkage with the inorganic substrate.

The aim of this work is the analysis of the mechanical behavior of basalt fibre-epoxy composite materials' from micro to macro-scale. The last decade basalt fibres have generated substantial interest and attention as reinforcing materials [5]. The interest in the basic and applied research of these fibres leads on their unique chemical properties (resistance to corrosive media) and; good thermal and mechanical performance [6]. As previously explained, the mechanical properties resulting from any reinforced material strongly depend on the nature of the fibre-matrix interface. Hence three different alkoxysilane coupling agents were used to analyze their adhesion efficiency between the basaltic reinforcement and the epoxide matrix and their influence on the final composite tensile and flexural behavior. The micromechanical method used to determine the fibre/matrix adhesion was the microbond test, widely used to characterize the adhesion level of thermoset composites. Besides, the influence of the different sizing treatments on the basalt fibres strength has been determined by monofilament tensile tests and Weibull two-parameter statistical analysis.

2 Materials and testing methods

2.1 Materials and treatments

The basalt fibre fabric used was a woven unidirectional plain supplied by Basaltex-Flocart and named BAS UD 280.1350.P. Its surface density was 280 g/cm^2 with 90% of the fibres oriented in the warp direction with a diameter of 20 μm, and the other 10% of the fibres oriented in the weft direction with a diameter of 10 μm. The analysis was focused on the filaments and composites that correspond to the warp direction. Finally, the unidirectional plain was supplied with a sizing compatible with epoxide resins but of unknown composition.

The basalt fibres have been used in 5 different conditions: with the original sizing (O-BF), unsized (U-BF), sized with γ-aminopropyltriethoxysilane (A-BF), with γ-glycidoxypropyltrimethoxysilane (G-BF) and with γ- methacryloxypropyltrimethoxysilane (M-BF), all of them from Sigma-Aldrich. To remove the surface sizing agents from the as received basalt unidirectional plain, the reinforcement was immersed in an acetone bath for 6 h at room temperature and washed in distilled water at constant stirring three times 5 min each. The unsized plain was first oven-dried at 60ºC for 3 days and then at 100ºC for 3 h. Scanning electron micrographs of the fibres were performed in a Jeol JSM-6380LA in order to evaluate the efficiency of the fibre sizing removal process.

The sizing elimination process was followed by the application of several coupling agents. The interaction of silane coupling agents with fibres may proceed through a few steps. First of all, the silane monomers have to be hydrolyzed in the presence of water and a catalyst (acid or

base) releasing alcohol and rising the reactivity of silanol groups. During this hydrolysis process the condensation of the silanols also takes place but at this stage, this process should be slowed down in order to leave free silanols to be adsorbed by the hidroxyl groups of the fibre. Thus, the silanol monomers are adsorbed via the hydroxyl groups of the fibre by hydrogen bonding and the free silanols are also adsorbed and react with each other forming a rigid polisiloxane network bonded with a stable –Si-O-Si- bond. Finally, and under heating conditions, the hydrogen bonds between silanols and hydroxyl groups of the fibres become covalent bonds (-Si-O-C-) liberating water, while residual silanols will further condense with each other[7].

Bisphenol-A type epoxy resin (D.E.R.™ 331™, from The Dow Chemical Company) and its hardener (4,4'-Diamine-diphenylmethane (DDM), from Sigma-Aldrich) were used as matrix system with a stoichiometric mixture ratio (1:1). This epoxide system curing kinetics and the final material glass transition temperature was analyzed by differential scanning calorimetry in a TA Instruments DSC Q2000.

2.2 Monofilaments tensile test and Weibull two-parameter statistical analysis

Basalt monofilaments test were carried out using a Zwick 005 universal machine with 20 N load cell, at a gauge length of 25 mm, 2 mm/min cross velocity, 50% relative humidity and at 25ºC. The monofilaments obtained from the yarns in warp direction of the unidirectional plain (O-BF, U-BF, A-BF, G-BF and M-BF samples) were stuck on the center of individual cardboard templates and their diameter was measured on an Olympus U-CMAD3 optical microscope. Three measurements were made for each fibre to calculate the average diameter, and the minimum number of samples tested for each batch was 35. Afterwards, the specimens were clamped to the testing machine and before the test began the cardboard templates were cut. The maximum peak load, maximum stress, elongation at break and tensile modulus were evaluated.

Basalt filaments brittleness, flaws and other imperfections lead to significant variations on their tensile strength data. Hence, a statistical analysis of these results was done determining the most popular statistical distribution, based on the two-parameter Weibull cumulative distribution function (CDF), F, described by Equation 1:

$$F\left(\sigma,\sigma_0,m\right)=1-\exp\left(-\left(\frac{\sigma}{\sigma_0}\right)^m\right) \tag{1}$$

The Weibull CDF describes the probability of fibre failure at a stress level less than or equal to σ. The probability density function (PDF), f, of this distribution is expressed by Equation 2:

$$f=\frac{m}{\sigma}\left(\frac{\sigma}{\sigma_0}\right)^m\exp\left[-\left(\frac{\sigma}{\sigma_0}\right)^m\right] \tag{2}$$

where σ_0 and m, from Equations 1 and 2, are the Weibull scale and shape parameters respectively, and the σ is the stress level at which failure occurs. The shape parameter describes the spread in strain to failure for the particular fibre and the scale parameter corresponds to the mean failure strain of the fibre. One of the most used methods to calculate the Weibull parameters is the least-squares. It allows the calculation of the parameters by the double logarithm transformation of the cumulative distribution. This transformation enables the conversion of the cumulative function into a linear regression equation. Applying normal logarithms to equation 1, a linear equation with the form y=mx-b is obtained as show in Equation 3:

$$\mathrm{Ln}\left[-\mathrm{Ln}(1-\mathrm{F})\right] = m\mathrm{Ln}(\sigma) - m\mathrm{Ln}\sigma_0 \tag{3}$$

Thus, a plot of $\mathrm{Ln}\left[-\mathrm{Ln}(1-\mathrm{F})\right]$ against $\mathrm{Ln}(\sigma)$ yields a straight line. The parameter m is obtained from the slope of the plot and σ_0 is calculated using the least-squares intercept and the slope (m). Thereby, the shape parameter can be considered the Weibull modulus and the scale parameter the characteristic strength [8].

According with the literature [9] this analysis method can also be useful to determine and estimate the changes on fibres tensile strength due to surface modifications, such as, unsizing or sizing processes. Thereby, at the present work the tensile data for each condition will be controlled by means of monofilament tensile test and afterward Weibull two-parameter statistical analysis.

2.3 Microbond Test

Microbond test is one of the several micromechanical methods used to estimate single fibre polymeric composite interfacial adhesion. It consists on depositing a micro-droplet of liquid resin onto the fibre (see Figure 1) and after the resin has been cured, force is applied to one of the extremes of the fibres in order to pull it out from the droplet. The load and displacement are recorded and the interfacial shear stress (IFSS) can be calculated by means of Equation 4:

$$\tau = \frac{F}{\pi d L} \tag{4}$$

where τ is the IFSS, F is the pull out tensile force (peak load), d is the fibre diameter and L is the embedded length.

The same card frames used in the single fibre tensile test were employed as sample holders for the microbond test. After applying the resin micro-droplet to the fibre and curing it, the embedded length, droplet and fibre diameters were measured using an Olympus U-CMAD3 optical microscope. Microbond test were performed in the same universal machine used for monofilaments tensile test with a load cell of 20 N and a crosshead speed of 2 mm/min. The free end of the fibre was held with a testing grip and the microdroplet was restrained by using two blades, the separation of which was controlled by a micrometer.

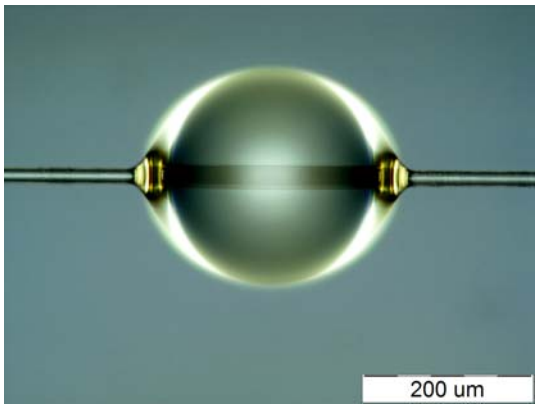

Figure 1. Optical microscope image of epoxide droplet onto original sized basalt fibre.

2.5 Composites preparation

Epoxy based composites reinforced with unidirectional basalt fibres were manufactured by compression molding process. The unidirectional reinforcement's several plies were placed into the mold and the epoxide system was poured on them and pushed in order to wet the fibres. The mold was closed and the whole compression process conditions can be seen in Figure 2. The sheets dimension was 160 x 160 x 2 mm and the fibre mass fraction in the obtained composite was 40%. The plates were then machined to the required macro-mechanical test samples dimensions.

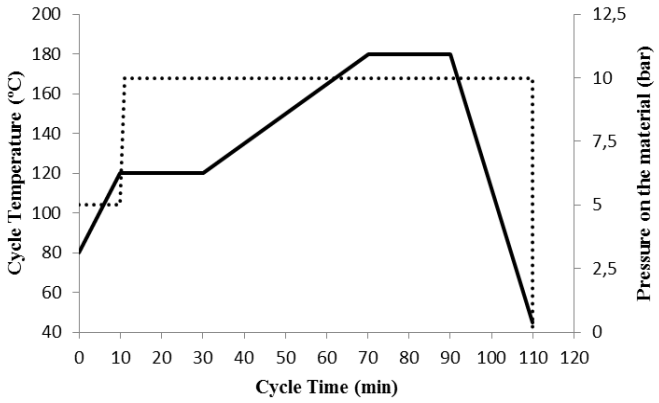

Figure 2. Schematic representation of the compression molding process (the solid line represents the temperature ramp along time and the dashed line represents the evolution of the pressure applied to the material).

2.7 Tensile and flexural tests

The macro-mechanical characterization of the composites were made either by tensile and flexural (three-point bending) tests, which were carried out in a Zwick 050 universal machine with a force cell of 50 KN. In tensile tests 2 mm/min of crosshead speed was used for samples with 120 mm length, 20 mm width and 2 mm thickness and; the maximum tensile stress, elongation at break and elastic modulus were determined. Besides, in flexural tests, the

crosshead speed was 3 mm/min, calculated in accordance with the UNE-EN ISO14125 standard and the samples dimensions were 60 mm length, 15 mm width and 2 mm thickness, being the span for the three-point flexural testing of 40 mm. The flexural strength and modulus were calculated.

3 Results and discussion

3.1 Sizing removal method efficiency and micro-mechanical analysis

Figure 3a shows that original sized basalt fibres are defined by smooth surfaces with few flaws and impurities. Unsized fibre surfaces, however, appeared to be damaged and partially covered with what may be remaining sizing as can be observed in Figure 3b. After acetone immersion part of the sizing was removed exposing the flaws previously healed by the commercial sizing. Hence, it can be concluded that the sizing was removed, to an extent, from the basalt fibre surface.

According with previous explanations, Figure 4a shows that the basalt monofilaments tensile results are highly scattered; Figure 4b shows Weibull two-parameter statistical analysis. It is noticed the good agreement of the experimental data of O-BF with the Weibull distribution (correlation coefficient of 0.988). The Weibull shape parameter (m) was 5.324, the slope of the regression line plotted in the figure and the scale parameter (σ_0) was 2104 MPa.

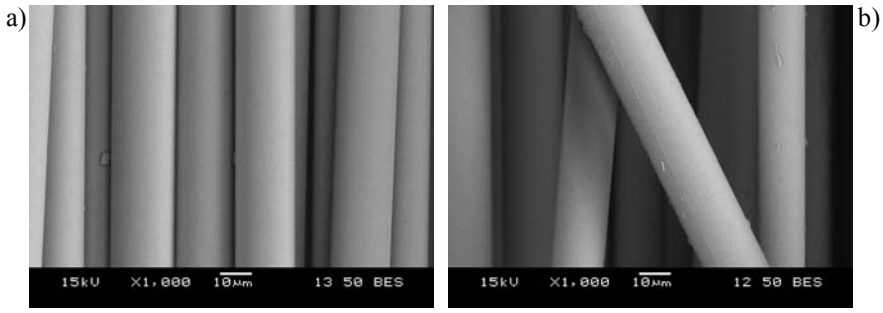

Figure 3. SEM images for a) original sized basalt fibres (O-BF) with smooth surfaces; b) .unsized basalt fibres (U-BF) with rough surfaces.

A plot of peak force vs. embedded area is shown in figure 5 for the data set of O-BF (Figure 5a) and U-BF (Figure 5b). They show how the microbond results for IFSS in both cases also tend to have high dispersion. According with Equation 4, a straight line is fitted to the data and forced to pass from the origin, resulting in an IFSS of 17.7 MPa and 12.5 MPa for O-BF and U-BF respectively. Lower IFSS values were expected for the unsized fibre case due to the worse interfacial adhesion comparing with O-BF. But taking into account the little difference on IFSS values obtained and that the data points fall on the straight line with significant scatter, the IFSS values resulting from this microbond test have to be considered of low accuracy.

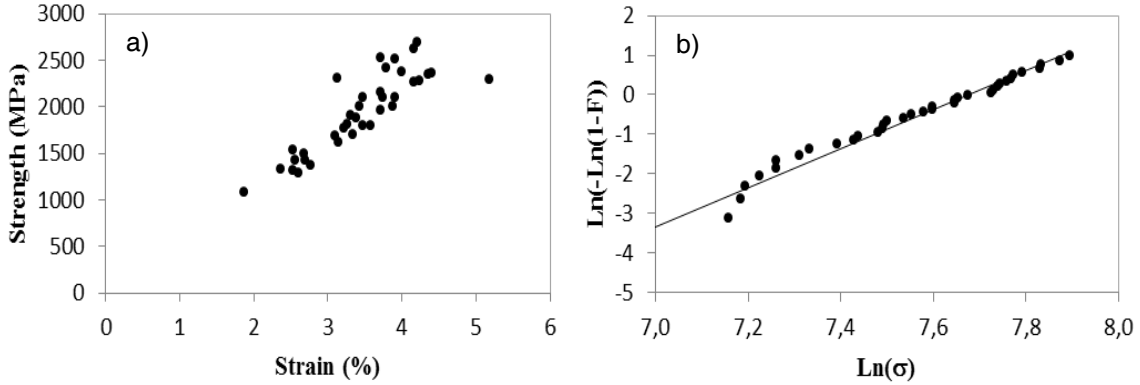

Figure 4. a) O-BF monofilaments tensile results plot; b) strength distribution approximation by Weibull two-parameter distribution.

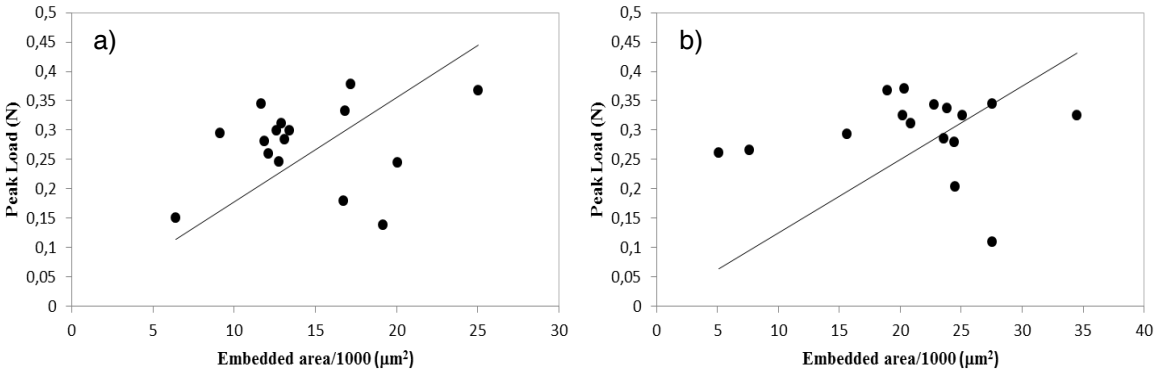

Figure 5. Plot of peak force vs. embedded area measured for; a) O-BF using microbond test; b) U-BF using microbond test.

3.2 Epoxy based unidirectional basalt fibre reinforced composites macro-mechanical analysis

In Table 1 the tensile and flexural results for unreinforced epoxy system (EP), O-BF and U-BF composites are summarized.

Sample		***Tensile Test***			***Flexural Test (three-point bending)***	
		σ_T (MPa)	**ε_T (%)**	**E_T (GPa)**	**σ_F (MPa)**	**E_F (GPa)**
EP	Average	64.40	7.80	1.50	93.10	2.75
	St. Dev.	*6.70*	*1.46*	*0.01*	*12.25*	*0.22*
EP/O-BF	Average	404.80	6.90	8.60	357.30	10.46
	St. Dev.	*36.60*	*0.35*	*0.30*	*67.79*	*1.04*
EP/U-BF	Average	398.20	7.30	8.40	361.05	11.50
	St. Dev.	*37.20*	*0.70*	*0.40*	*18.02*	*0.76*

Table 1. Summary of the tensile and flexural results for unreinforced EP, O-BF and U-BF composites.

As expected, tensile and flexural strength and modulus increase in high extent when the neat matrix was reinforced with the basalt fibre. However, it also was expected to notice differences between both composite types and it has not been thus. Moreover, the original sized and unsized composites show almost the same mechanical behavior, when what was

thought to obtain worse overall mechanical results for the case of unsized composite, due to the poorer interface adhesion between the matrix and reinforcement.

4 Conclusions

The little difference in interfacial shear stress results obtained for unsized and original sized basalt fibres and the equal macro-mechanical results obtained for both composite types, suggested a misunderstanding on the adhesion mechanism between the basalt/epoxy system. SEM images confirm the fibres surface treatment removing; thus, it is expected to get lower IFFS and tensile and flexural strengths for unsized fibres composites. Hence, to clarify such an unexpected behavior a further research on the sizing elimination efficiency would be helpful by means of fibres' surface chemical analysis and SEM analysis on composite samples breaking surfaces. Besides, it would also be advisable to make U-BF monofilament tensile tests to observe possible differences in its Weibull two-parameter distribution respect to O-BF. Silane coupling agent has not been applied yet due to the uncertainty on the sizing removal process. Finally, in microbond tests it is usual to obtain large scatter in the test data something that could be attributed to testing parameters like droplet size and position of the microdrop in the loading fixture, factors that are difficult to control.

References

[1] Hull D. *An introduction to composite materials*. Cambridge University Press, London, (1996).
[2] Plonka R., Mäder E., Gao S.L., Bellmann C., Dutschk V., Zhandarov S. Adhesion of epoxy/glass fibre composites influenced by aging effects on sizings. *Composites: Part A*, **35**, pp. 1207–1216 (2004).
[3] Czigány T., Deák T., Tamás P. Discontinuous basalt and glass fiber reinforced PP composites from textile prefabricates: effects of interfacial modification on the mechanical performance. *Composite Interfaces*, **15**, pp. 697–707 (2008).
[4] Pantoja M., Díaz-Benito B., Velasco F., Abenojar J., del Real J.C. Analysis of hydrolysis process of g-methacryloxypropyltrimethoxysilane and its influence on the formation of silane coatings on 6063 aluminum alloy. *Applied Surface Science*, **255**, pp. 6386–6390 (2009).
[5] Czigány T., Vad J., Pölöskei K. Basalt fiber as a reinforcement of polymer composites. *Periodica Polytechnica Ser. Mech. Eng*, **49**, pp. 3–14 (2005).
[6] Novitskii A.G. High-temperature heat-insulating materials based on fibers from basalt-type rock materials. *Refractories and Industrial Ceramics*, **45**, pp. 144-146 (2004).
[7] DiBenedetto A.T. Tailoring of interfaces in glass fiber reinforced polymer composites: a review. *Materials Science and Engineering:A*, **302**, pp. 74–82 (2001).
[8] Placet V. Characterization of the thermo-mechanical behaviour of Hemp fibres intended for the manufacturing of high performance composites. *Composites: Part A*, **40**, pp. 1111-1118 (2009).
[9] Park J. M., Shin W-G, Yoon D-J. A study of interfacial aspects of epoxy-based composites reinforced with dual basalt and SiC fibres by means of the fragmentation and acoustic emission techniques. *Composites Science and Technology*, **59**, pp. 355-370 (1999).