Properties of composite laminates based on basalt fibers

with epoxidized vegetable oils

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Abstract

This paper deals with the development of polymeric materials derived from epoxidized vegetable oils which have been used in the manufacture of laminated composite materials with basalt fabrics. Epoxidized linseed oil (ELO) and epoxidized soybean oil (ESBO) were used as biobased matrices. The basalt fabrics were modified with amino-silane and glycidyl-silane to increase fiber-matrix interactions. The curing behaviour of both resins was evaluated by differential scanning calorimetry (DSC) and oscillatory rheometry (OR). The evaluation of mechanical properties was made by tensile, flexural and Charpy tests. The extent of the fiber-matrix interactions among interface was evaluated by scanning electron microscopy (SEM). The obtained results revealed that surface modification of basalt fibers with glycidyl-silane clearly improves the mechanical properties of the composites. The use of the ELO resin as matrix for

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composite laminates improved substantially the mechanical performance compared to composites made with ESBO.

Keywords: basalt fibres; epoxidized vegetable oils; silanes; mechanical characterization.

1.- Introduction.

Composite materials with polymer matrices have traditionally been made with petroleum-based thermosetting resins. Moreover, the use of polymeric materials from non-renewable fossil resources is continuously increasing and there is a growing society awareness for the conservation of the environment, making it necessary the development of polymeric materials and composites made from renewable resources in order to minimize the environmental impact. For this reason, and following promotion from authorities and public bodies, the potential of renewable resources to displace or replace petrochemical-based polymers has attracted the attention of many researchers [1-6]. Vegetable oils are good candidates for polymer precursors since they are composed of triglycerides with three fatty acids linked to a glycerol molecule. Most common oils contain fatty acids whose length varies between 14 and 22 carbon atoms with 0 to 3 carbon-carbon double bonds per fatty acid. The double bonds in triglycerides offer the opportunity to modify their chemical structure in order to make them more reactive. Therefore, it is possible to obtain different products such as epoxidized vegetable oils (EVO), maleated vegetable oils (MVO) or hydroxylated vegetable oils (HVO) as base materials for polymer synthesis and/or manufacturing [4]. The epoxidation of vegetable oils introduces oxirane rings into carbon-carbon double bonds in fatty acids by conventional epoxidation with peracids; this is one of the most
important oil functionalization processes known for many years [7, 8]. It is possible to
crosslink epoxidized vegetable oils with typical crosslinking agents or hardeners for
epoxies such as amines [9] and anhydrides [10]. Epoxidized vegetable oils, such as
epoxidized soybean oil (ESBO), epoxidized linseed oil (ELO), epoxidized canola oil
and epoxidized castor oil, among others, have been successfully used to prepare
thermosetting polymers and composite materials [4, 5, 10-13].

Glass, carbon and aramid fibers are widely used in composite manufacturing due
to their high performance, but they are expensive and their use causes a high
environmental impact. This is why in recent years, composites reinforced with natural
fibers have been increasingly developed [14-17]. However, the mechanical properties of
natural fibers are usually far from those provided by conventional glass, carbon or
aramids and this fact restricts their use in applications where high mechanical properties
are required. Glass fiber is, with difference, the most widely used reinforcement fiber
due to an excellent balance between properties and cost; in the last years other siliceous
fibers such as basalt and slate fibers have been tested as candidates for composite
manufacturing. Basalt fiber (BFs), obtained from the fusion of volcanic rocks, is a good
alternative to reinforce polymeric materials [18-20]. Its chemical composition is similar
to glass fibers, since basalt is mainly composed of Al$_2$O$_3$, SiO$_2$, CaO, MgO, K$_2$O, Na$_2$O,
Fe$_2$O$_3$ y FeO [21, 22] and it has better mechanical properties than vegetable fibers and
slightly higher than conventional glass fibers. In recent years, BFs fabrics have been
investigated as reinforcement in polymer composites and they have been compared to
composites made with glass fibers [17, 21, 23].

One key factor to obtain optimum mechanical properties of composite materials
is ensuring good interaction between the matrix and the reinforcement which allows the
load transfer from the matrix to the reinforcement. If the interaction is weak, there is no
continuity in the material and the matrix will bear most of the load, thus resulting in poor mechanical properties of the composite. In order to improve the interaction between the fiber and matrix the surface of the reinforcement can be functionalized by plasma treatment [24-26], or by the use of coupling agents such as amines [27, 28] or silanes [18, 29]. The effectiveness of silanes on glass fiber has been widely studied; as basalt fiber is a siliceous fiber, silanization is an interesting choice to improve fiber-matrix interactions.

This paper intends to evaluate the efficiency of different silane (amine and glycidyl) coupling agents in composite laminates of basalt fabrics with two different epoxidized vegetable oils (epoxidized linseed oil-ELO and epoxidized soybean oil-ESBO). The curing behaviour of the thermosetting resins is studied by differential scanning calorimetry (DSC) and gel-time is determined by oscillatory rheometry (OR). Laminate composites with basalt fabrics with different coupling silane agents and ELO and ESBO are manufactured using resin transfer moulding (RTM) and the effect of the silane treatment on mechanical properties of all composites are evaluated by tensile, flexural and impact tests. Interface phenomena are followed by scanning electron microscopy (SEM).

2.- Experimental.

2.1.- Materials.

Two types of commercial epoxidized vegetable oils were used as biobased epoxy matrices: epoxidized linseed oil (ELO) with an epoxide equivalent weight (EEW) of 178 g equiv\(^{-1}\) and epoxidized soybean oil (ESBO) with an epoxide equivalent weight of 238 g equiv\(^{-1}\); both epoxidized oils were supplied by Traquisa SA (Madrid, Spain). Liquid methyl nadic anhydride (MNA) was used as crosslinking agent; this product has
an anhydride equivalent weight (AEW) of 178.2 g equiv\(^{-1}\) and it was supplied by Sigma-Aldrich (Schnelldorf, Germany). The following resin formulation was used: the EEW:AEW ratio was set at 1:0.9; propanediol (PDO) (1 wt.%) food grade was used as initiator of the crosslinking reaction and it was supplied by Coralim Additives (Ribaroja Turia, Spain) and finally, 1-methyl imidazole (1MI) (2 wt.%) was used as accelerator and it was supplied by Sigma-Aldrich (Schnelldorf, Germany).

A basalt fabric with a surface density of 940 g m\(^{-2}\) reference BAS 940.1270.T, supplied by Basaltek (Basaltek, Wevelgem, Belgium) was used as reinforcement. Two different silanes were used for surface modification and both were supplied by Sigma Aldrich (Schnelldorf, Germany). The silane with amine functionality was [3 - (2-aminoethylamine) propyl]-trimethoxysilane (Silane A) and the other one was glycidyl trimethoxysilane [2 - (7-oxabicyclo [4.1.0] hept-3-yl) ethyl] silane (Silane B). Scheme 1 shows the chemical structures of the different components used for thermosetting formulation as well as silanization. With regard to epoxidized linseed oil (ELO) and epoxidized soybean oil (ESBO), Scheme 1 shows the theoretical structures obtained after full conversion of carbon-carbon double bonds into oxirane rings. Usually, full conversion is not achieved and on the other hand, some other parallel reactions (i.e. homopolymerization) can occur thus leading to slightly different chemical structures.

Scheme 1

2.2.- Silane treatment of basalt fibers.

Before applying the treatment with silanes, basalt fabrics were heated in an oven at 300 °C for 2 hours in order to remove previous organic sizings. The silanes (1 wt.%) were diluted in a water acetone solution (volume ratio 50:50) and basalt fabrics were
immersed in the solutions for 1 hour and finally they were washed with distilled water and dried at room temperature for 24 hours. Three types of basalt fabrics were obtained: basalt fabric with thermal treatment is referred as Basalt TT, basalt fabric treated with amino-silane, which is referred to as Basalt A, and finally basalt fabric treated with glycidyl-silane which is referred as Basalt B.

2.3.- Composite manufacturing.

The manufacturing of composite laminates was carried out using a resin transfer moulding (RTM) process in a Hypaject MKII machine (Plastech Thermoset Tectonics, Gunnislake, UK). A vacuum pump was connected in the vent hole of the mould in order to improve the air evacuation and to avoid bubble trapping in the laminate. The processing conditions for composite laminates are summarized in Table 1. Four basalt fabric layers were stacked in the same directions (0/90°) for composite manufacturing. The total fiber content was close to 57 wt.% (57.3 wt.% for composites with epoxidized linseed oil-ELO and 56.2 wt.% for composites with epoxidized soybean oil-ESBO).

Table 1

2.4.- Characterization of the curing process.

The study of the curing process of epoxidized vegetable oils (ELO and ESBO) was performed using dynamic differential scanning calorimetry in a Mettler Toledo DSC 821e (Mettler Toledo SAE, Barcelona, Spain) under nitrogen atmosphere. The first step of thermal heat program consisted in heating from 30 to 300 °C at a heating rate of 5 °C min\(^{-1}\). Then cooling was performed from 30 °C to -10 °C min\(^{-1}\) and finally a second heating was performed from 30 °C up to 350 °C at 5 °C min\(^{-1}\).
Additionally, the isothermal curing of the epoxidized vegetable oils was also followed by plate-plate oscillatory rheometry in an AR-G2 (TA Instruments, New Castle, USA). The analysis was conducted using a configuration of two parallel plates \((D = 25 \, \text{mm})\). Four different isothermal temperatures \((90, 100, 110, \text{and } 120 \, ^\circ\text{C})\) were used until it was observed that the material was fully cured \((\delta = 0^\circ)\). The controlled variables were 0.1\% strain \((\gamma)\) at a constant frequency of 1 Hz.

2.5.- Mechanical testing.

Tensile tests were conducted on a universal testing machine Instron Model 3382 with a load cell of 100 kN and a crosshead rate of 2 mm min\(^{-1}\); all tests were performed according to ASTM D3039-08. Flexural tests were performed on a universal testing machine model LLOYD 30 K with a load cell of 500 N and a crosshead rate of 1.7 mm min\(^{-1}\) according to ASTM D790-10. Impact tests were performed according to ISO 179 standard, using a 6 J Charpy impact pendulum (Metrotec SA, San Sebastian, Spain). Five different samples were tested for each characterization test and average values were calculated.

2.6.- Microscopic analysis of the fractured surfaces.

The analysis of the fractured surfaces was performed with cryofractured (in liquid nitrogen) samples; then samples were coated by gold sputtering and finally they were observed by scanning electron microscopy (SEM) in a Phenom SEM (FEI Company, Eindhoven, The Netherlands) at an acceleration voltage of 5 kV.

3.- Results and discussion.

3.1.- Characterization of the curing process of epoxidized vegetable oils.
The curing of the two biobased epoxy resins (ELO and ESBO) was followed up with dynamic differential scanning calorimetry (DSC); curing temperature and time are key parameters since a proper curing of the resin is one of the main issues to be considered in order to obtain composites with good properties. The main calorimetric parameters obtained from the corresponding calorimetric (DSC) curves of both resins can be observed in Table 2. Curing of ELO resin proceeds with a maximum reaction rate located at 175.7 ºC. No residual heat is released in the second heating step so that, the material is fully cured. With regards to curing of epoxidized soybean oil (ESBO) the maximum curing rate (temperature peak) is moved to higher temperature (183.2 ºC) and no residual released heat is detected in the second heating step thus indicating full curing during the first heating. The glass transition temperature is not easy observable in the second heating program. In addition, the exothermicity of the two crosslinking processes is different with values of 118.9 J g\(^{-1}\) for epoxidized linseed oil (ELO), and 91.4 J g\(^{-1}\) for epoxidized soybean oil (ESBO). These values are in total agreement with the chemical structure of both epoxidized vegetable oils. Epoxidized linseed oil is characterized by an EEW of 178 g equiv\(^{-1}\) while epoxidized soybean oil has an EEW of 238 g equiv\(^{-1}\). These values indicate that for a similar molecular weight of the vegetable oil, ELO has more epoxide groups than ESBO. For this reason, ELO reactivity is higher and, consequently, the exothermicity is higher.

**Table 2**

The curing gel time of both epoxidized vegetable oils at different temperatures in the 90-120 ºC range was determined using plate-plate oscillatory rheometry by following the evolution of the phase angle (δ). Initially phase angle values are close to
90° which is representative for liquids thus indicating that when a sinusoidal (dynamic) stress is applied to a liquid, the corresponding response (elongation-deformation) also follows a sinusoidal type but delayed by 90° with regard to the applied stress. The crosslinked resin behaves as an elastic solid material and is characterized by a phase angle of near 0° (this means no phase angle between the applied dynamic stress and the corresponding dynamic deformation). The phase angle decreases as the curing process starts and the phase angle is close to 0° when the resin is fully cured; the gel time can be defined as the midpoint between a fully liquid state and the fully cured crosslinked resin with (elastic solid); as the phase angle changes from 90° (liquid) to 0° (elastic solids), the gel time can be defined as the time to reach a phase angle of 45° which, in turn, implicate that the storage modulus (G’) and the loss modulus (G”') are identical (crossover point). Fig. 1 shows the phase angle as a function of time for the isothermal curing of both epoxidized vegetable oils (ELO and ESBO). In both cases, it can be clearly seen that the gel time (δ = 45°) occurs at lower times as temperature increases. The minimum value is reached at a temperature of 120°C with gel time values of 1497 s for ELO and 2750 s for ESBO. These results indicate that curing of ELO requires less time than ESBO due to the higher EEW of ELO if compared to ESBO. Table 3 summarizes the gel time for both epoxidized vegetable oils at different temperatures.

**Figure 1**

**Table 3**

By considering the data obtained by differential scanning calorimetry (DSC) and oscillatory rheometry (OR) it was decided that 100 ºC is a proper temperature for crosslinking both epoxidized vegetable oils since balanced curing cycles can be
designed (moderate temperatures and moderate curing times). At 120 °C the curing in both resins starts very fast and it can produce problems in the filling process by RTM during composite laminate manufacturing. Regarding the epoxidized soybean oil (ESBO) thermosetting resin, it is important to remark that it needs longer curing time as it is characterized by a lower reactivity than the epoxidized linseed oil (ELO).

3.2.- Mechanical characterization of basalt-EVO composite laminates.

Fig. 2 shows the tensile behaviour of basalt-EVO composites; the tensile moduli do not vary significantly with the use of the two different silanes in comparison to untreated basalt fabrics. However the tensile strength increases significantly in composites with basalt fabrics subjected to silanization, independently of the epoxidized vegetable oil used as composite matrix. In both resins the highest value for tensile strength is obtained with the basalt fabrics previously treated with the glycidyl-silane (Silane B). In the case of composites manufactured with ELO matrix and basalt fabrics subjected to prior silanization with glycidyl-silane, a clear increase in tensile strength is observed from 330.8 MPa (not silanized basalt fabric, only with thermal treatment to remove previous sizing, ELO-Basalt TT) up to 366.2 MPa which represents a percentage increase of 10.7%. In the case of epoxidized soybean oil (ESBO), a similar increase is detected from 288.8 MPa (ESBO-Basalt TT) up to 328.6 MPa (percentage increase of about 13.8%) for composite laminates with previous glycidyl-silane treatment.

Figure 2
A comparison of the flexural properties of basalt-EVO composite laminates (Fig. 3) shows in a clear way a remarkable increase in both modulus and strength values for silanized basalt fabrics. These results indicate that once again, the glycidyl-silane (silane B) offers better mechanical performance than the amino-functionalized silane in both epoxidized vegetable oils although both silanes gives higher properties than untreated basalt fabrics. With regard to epoxidized linseed oil (ELO) as matrix for basalt composite laminates, the flexural strength of laminates with non-silanized basalt fabrics (ELO-Basalt TT) is of about 146.2 MPa and this value is substantially increased up to twice (300.2 MPa) in laminates with glycidyl-silane pre-treatment. This situation is more pronounced in composite laminates with epoxidized soybean oil (ESBO) in which, the flexural strength changes from 93.1 MPa (ESBO-Basalt TT) up to 238.9 MPa (ESBO-Basalt B) with previously glycidyl silanized basalt fabrics. With regards to flexural modulus, we can see a clear increase with the silane treatment with identical tendency of that observed in tensile strength.

Figure 3

Obviously, as epoxidized linseed oil (ELO) is characterized by higher EEW than epoxidized soybean oil (ESBO), crosslinked ELO gives stiffer materials than in the case of ESBO as ELO possesses more epoxide groups per oil molecule. If we compare the obtained results with other studies with composite laminates with similar weight percentage fiber content (mainly glass) and petroleum-based epoxy matrices, it is important to remark that basalt-ELO composites offer similar performance thus providing a high environmental efficiency solution for medium-high performance composite laminates [21, 30, 31].
Table 4 shows a summary of the results obtained in Charpy impact tests. Composites made with ESBO matrix absorb more energy than composites made with ELO matrix. This behaviour is due to the fact that ESBO has a lower crosslinking density than ELO leading to a more flexible network. Therefore, the obtained composites are less resistant but they are more ductile and therefore they can absorb more energy during the deformation and fracture processes. It can also be observed that the silane treatment on basalt fabrics improves the energy absorption.

Table 4

3.3.- Analysis of the fracture surface.

In addition to mechanical characterization, a morphological analysis of cryogenically fractured samples was performed in order to determine the degree of interaction between the basalt fiber and the epoxidized vegetable oil (EVO) matrix. Fig. 4 shows the SEM images corresponding to epoxidized linseed oil composites with basalt fabrics subjected to different silanes. Fig. 4a & 4b show the SEM images of basalt-ELO composite laminates without silane treatment (only thermal treatment to remove previous sizings). We can clearly see that the interaction between the fiber and the matrix is very poor, since there are gaps around the fiber; these gaps act as stress concentrators as they do not allow good load transfer from the matrix to the fiber; we can also observe that the longitudinal surfaces of the fibers are very clean, with no residual matrix which is representative for poor matrix-fiber adhesion. These facts indicate a lack of interaction between the fiber and the matrix limiting the strength of the laminate. However, Fig. 4c & 4d show the fracture surfaces of composites with ELO and amine-silanized basalt fabrics (ELO-Basalt A). We can clearly observe differences
with the above mentioned untreated basalt fabrics. The existing gaps have been substantially reduced and this has a positive effect on fiber-matrix continuity so that, load transfer occurs and the matrix is able to transfer almost all the stresses to the stiffer component. In the case of glycidyl-silanized basalt fabrics (Fig. 4e & 4f) we observe a similar morphology and it is evident that the silane treatment has improved fiber-matrix interactions and, as described previously, this has a positive effect on the overall mechanical performance.

In relation to composites with basalt fabrics and epoxidized soybean oil (ESBO) matrix, Fig. 5 shows SEM images for different treatments. Once again we observe the presence of gaps in the fiber surroundings in composites without silane treatment (Fig. 5a & 5b) thus indicating poor interactions which, in turn, are responsible for the low mechanical performance. Fig. 5c & 5d (ESBO-Basalt A) and Fig. 5e & 5f (ESBO-Basalt B) correspond to amine-silane and glycidyl-silane treatment on basalt fabrics respectively and we can clearly see an increase in adhesion between the fiber and the matrix, which is translated into an improvement of the mechanical properties as described before.

Figure 4

Figure 5

4.- Conclusions.

In this work the influence of the silane treatment on mechanical properties of composite laminates manufactured with two different biobased epoxy resins (epoxidized linseed oil-ELO and epoxidized soybean oil-ESBO) has been evaluated. Composites with these biobased epoxies can be manufactured by conventional RTM
process and, in general terms, composites with previous silane treatment on basalt fabrics offer better mechanical performance than untreated basalt fabrics. The best results are obtained using basalt fabrics modified with a glycidyl silane (trimetoxy [2-(7-oxabicyclo [4.1.0] hept-3-yl) ethyl] silane) with both ELO and ESBO matrices. Generally, composites made with epoxidized linseed oil (ELO) have better strength properties than ESBO composites; that is due to the fact that ELO enables a higher crosslinking density due to a higher equivalent epoxide weight (EEW) but, in contrast, composites manufactured with ESBO matrix have the ability to absorb more impact energy taking advantage of the lower crosslinking density compared to ELO. Silanization of basalt fibers highly improves fiber-matrix interactions as detected by SEM analysis. There is a lack of gaps between the fiber and the surrounding matrix, due to improved wetting properties. In general terms, both amino- and glycidyl- silanes contribute to improve mechanical performance of the manufactured composites with basalt fabrics, although slightly better results are obtained with glycidyl silanes.

Acknowledgements

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References


Figure legends

Scheme 1.- Chemical structure of chemicals used: a) epoxidized linseed oil (ELO, b) epoxidized soybean oil (ESBO), c) methyl nadic anhydride (MNA), d) propanediol (PDO), e) 1-methyl imidazole, f) [3 - (2-aminoethylamine) propyl]-trimethoxysilane and g) [2 - (7-oxabicyclo [4.1.0] hept-3-yl) ethyl] silane.

Figure 1.- Phase angle (δ) as a function of the curing time at different isothermal curing temperatures obtained by oscillatory rheometry (OR) for a) epoxidized linseed oil (ELO) and b) epoxidized soybean oil (ESBO), cured with methyl nadic anhydride (MNA).

Figure 2.- Comparison of the tensile properties of basalt-EVO composite laminates with different surface treatments.

Figure 3.- Comparison of the flexural properties of basalt-EVO composite laminates with different surface treatments.

Figure 4.- SEM images at 3000x (a, c and e) and 5000x (b, d and f) of ELO-Basalt TT samples (a & b) ELO-Basalt A (c & d) and ELO-Basalt B (e & f).

Figure 5.- SEM images at 3000x (a, c and e) and 5000x (b, d and f) of ESBO-Basalt TT samples (a & b) ESBO-Basalt A (c & d) and ESBO-Basalt B (e & f).
Table 1.- Processing conditions of epoxidized vegetable oil (EVO)-basalt fabric (BF) composite laminates by resin transfer moulding (RTM).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>ELO matrix</th>
<th>ESBO matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin Injection temperature (°C)</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>Resin injection pressure (kPa)</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>In mould cavity pressure (kPa)</td>
<td>95</td>
<td>95</td>
</tr>
<tr>
<td>Curing cycle</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Time (h)</td>
<td>3.0</td>
<td>3.5</td>
</tr>
<tr>
<td>Demoulding temperature (°C)</td>
<td>30</td>
<td>30</td>
</tr>
</tbody>
</table>
Table 2.- Main characteristics of the curing process of epoxidized linseed oil (ELO) with methyl nadic anhydride (MNA) and epoxidized soybean oil (ESBO) with MNA obtained by dynamical differential scanning calorimetry (DSC).

<table>
<thead>
<tr>
<th>Parameter [1st heating]</th>
<th>ELO-MNA</th>
<th>ESBO-MNA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Onset (ºC)</td>
<td>143.4</td>
<td>154.2</td>
</tr>
<tr>
<td>Endset (ºC)</td>
<td>231.2</td>
<td>233.4</td>
</tr>
<tr>
<td>Peak (ºC)</td>
<td>175.7</td>
<td>183.2</td>
</tr>
<tr>
<td>Enthalpy (J g⁻¹)</td>
<td>118.9</td>
<td>91.4</td>
</tr>
</tbody>
</table>
Table 3.- Characterization of the crossover point in which $G'=G''$ values of the isothermal curing by plate-plate rheometry of ELO & ESBO resins, for gel time determination.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>ELO matrix</th>
<th></th>
<th>ESBO matrix</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$G'=G''$ (Pa)</td>
<td>Time (s)</td>
<td>$G'=G''$ (Pa)</td>
<td>Time (s)</td>
</tr>
<tr>
<td>90</td>
<td>623</td>
<td>9453</td>
<td>565</td>
<td>17961</td>
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<tr>
<td>100</td>
<td>195</td>
<td>4560</td>
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<td>9008</td>
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<td>110</td>
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<td>2787</td>
<td>414</td>
<td>4309</td>
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<tr>
<td>120</td>
<td>171</td>
<td>800</td>
<td>96</td>
<td>2748</td>
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</table>
Table 4.- Values of Charpy impact energy for epoxidized vegetable oil (EVO)-basalt fabric (BF) composite laminates.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Silane type</th>
<th>Charpy impact energy (kJ m(^{-2}))</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>ELO-BasaltTT</td>
<td>--</td>
<td>116.5</td>
<td>1.9</td>
</tr>
<tr>
<td>ELO-BasaltA</td>
<td>amino</td>
<td>149.0</td>
<td>4.6</td>
</tr>
<tr>
<td>ELO-BasaltB</td>
<td>glycidyl</td>
<td>123.5</td>
<td>22.1</td>
</tr>
<tr>
<td>ESBO-BasaltTT</td>
<td>--</td>
<td>118.5</td>
<td>10.2</td>
</tr>
<tr>
<td>ESBO-BasaltA</td>
<td>amino</td>
<td>142.5</td>
<td>11.6</td>
</tr>
<tr>
<td>ESBO-BasaltB</td>
<td>glycidyl</td>
<td>151.5</td>
<td>7.6</td>
</tr>
</tbody>
</table>
a) epoxidized linseed oil (ELO)

b) epoxidized soybean oil (ESBO)

c) methyl nadic anhydride (MNA)
d) 1,2 propanediol (PDO)
e) 1-methyl imidazole (1-MI)

f) [3 - (2-aminoethyleamine) propyl]-trimethoxysilane
g) [2 - (7-oxabicyc[4.1.0] hept-3-yl) ethyl] silane