Physical and Mechanical Assessment of a Novel Hybrid Epoxy Composite Reinforced with Natural Fibers

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Abstract

Recently, using natural fibers as reinforcements in composites has attracted much attention. In this study, we employed Goat Hair Fibers (GHF) to fabricate hybrid composites with an effective matrix, which is reinforced with Pine Cone micro-Fibers (PCF). Assessment of mechanical performance of composites and fibers plus scanning electron microscopy (SEM) studies demonstrated that both fibers enhance the mechanical properties of composites owing to their good mechanical characteristics and compatibility with the matrix. SEM studies and comparison of measured tensile and flexural modulus with the computed theoretical values by using modified Cox theory revealed that the performance of PCF interface is better than that of GHF due to the presence of lignin in PCF. Furthermore, PCF in hybrid composites has led to amendment of GHF-matrix interface. Investigation of the water absorption mechanism using experimental data and calculated diffusion coefficient values also proved the interface behavior of fibers.

Keywords: Natural Fibers, Hybrid Composites, Effective Matrix, Mechanical Properties

1- Introduction

Recent years have been witnessed the growing demand for polymer composites due to their excellent properties such as specific strength, wear resistance, and environmental durability. However, beside their remarkable benefits they represent some disadvantages such as environmental damage and high production costs. An influential approach to lessen these drawbacks is the substitution of synthetic components of composites with natural ones, since they offer more advantages over artificial reinforcements such as low cost, abundance, less manufacturing requirements, less health risk, and great recyclability and biodegradability. Therefore, fabrication and application of natural fiber reinforced composites has recently attained much consideration. [1–3]

Natural fibers can be divided in two groups of plant-based fibers and animal-based fibers. Plant-based fibers are usually obtained from plants and crops such as bagasse, hemp, flax, and jute that are numerously applied in recent researches [4]. Examples of animal-based fibers are sheep-wool [5], feather [6], and hair [7]. The problem that has always been associating with natural fibers especially cellulose is their inherent hydrophilic character and weak interface with matrix due to existence of polar Hydroxyl (OH) group in cellulose that leads to high water absorption and low compatibility and consequently adverse influence on mechanical performance [2,8].

Pine Cone Fiber (PCF) as a highly obtainable natural fiber includes cellulose that allows us to take its advantages. Nevertheless, PCF contains significant amount of lignin as well, that can alleviate some of problems caused by cellulose [9]. Lignin contains polar groups in addition to non-polar ones, which could contribute to improvement of water absorption behavior. Besides, lignin is renewable and biodegradable that can remarkably increase tensile strength and modulus of composites [2]. Considering hemicellulose as non-

desirable component in many plant-based fibers, it is crucial to reduce the hemicellulose content by applying fiber preparation treatments [10]. Among different treatment methods, here we used mercerization to increase cellulose content and reduce hemicellulose [11]. It is worth commenting that enough attention needs to take into account to carefully adjust the hemicellulose content while remaining acceptable amount of lignin.

Regarding that nomads in Iran have been making their highly durable tents, and some of their life necessities like cloths and ropes from goat's hair. This made us think that goat's hair can be an appropriate candidate for reinforcing composites. Therefore, Goat Hair Fiber (GHF) as an animal based natural fiber can represent especial characteristics such as good mechanical properties, particular surface topography, and high resistance against solar heat and radiation. Considering the advantages of GHFs and PCFs, it was decided to benefit the most from both mentioned fibers as animal-based and plant-based fibers in hybrid composites.

Hybrid composites compose a mixture of two or more reinforcements in a matrix. In terms of natural and artificial fibers, there are three possible combinations of hybrid composites consisting artificial-artificial [12], artificial-natural [13] and natural-natural [14] fibres. With due attention to drawbacks of artificial fibers, numerous researches have been recently implemented in fabrication and studying the new hybrid composites via substitution of artificial fibers with naturals. For example, M. Boopalan and coworkers [15] investigated and compared the mechanical and thermal behaviors of raw jute and banana fiber reinforced epoxy hybrid composites with different weight fraction of fibers using molding technique. They reported that the addition of banana fibers to jute/epoxy composites of up to 50% by weight caused an increase in mechanical and thermal properties but a decrease in moisture absorption property. In another study, M. Jawaid and co-workers [16] reported that tensile and flexural performance of tri layer oil palm empty fruit bunches/woven jute fibers reinforced epoxy hybrid composites improved by hybridization in such a way that tensile and flexural properties of hybrid composite is higher than that of empty fruit bunches composites but less than woven jute composite. In a new work, D.K.K. Cavalcanti et al. [17] investigated the effect of hybridization and chemical treatments on the mechanical properties of a natural fiber hybrid composite fabricated with incorporating jute, sisal and curauá fibers within epoxy. They stated that the tensile, flexural and impact properties significantly improved by addition of the natural fibers to pure jute-based composites. The results showed that the fiber treatments had different effects on the mechanical properties of the hybrid composites.

According to literature, main factors influencing the mechanical behavior of hybrid composites are the types, size, volume fraction, and treatment of fibres [17–21], and the combinations of micro and macro-sized reinforcements in hybrid composites can significantly enhance the composite properties. In fact, the micro sized reinforcement can contribute to making an effective matrix with improved properties, while the second component reinforces the effective matrix. Like the work performed by Senturk and co-authors [19] in which they filled the polypropylene matrix with calcite particles to form an effective matrix and then reinforced that with short glass fibers. We have it on good authority that, no natural hybrid composite containing micro and macro-sized fibers and effective matrix has been manufactured so far. Therefore, present research aims to improve mechanical and physical properties of epoxy resin by

incorporating two micro and macro-size natural fibers. For this purpose, PCFs added in different volume fractions to resin epoxy to produce an effective matrix. In addition, effective matrixes as well as resin epoxy were reinforced with two different volume percent of GHF as macro fibers. In the following, several mechanical and physical tests beside Scanning Electron Microscopy (SEM) analysis were conducted to obtain the optimum fraction of each reinforcement and to investigate the interface properties plus the efficacy of processing parameters on hybrid composites performance.

2- Experimental

2-1- Materials

In this study the laminating low viscosity epoxy resin PC105 (η~ 2900 mPa.s, density ~ 1.17 g/cm3) and the slow hardener 520 (η =25 mPa.s, density 1.0 g/cm3) were mixed and cured based on the technical data sheet (resin: hardener (100:20), η~ 1200 mPa.s, specific gravity 1.16, pot life 60 min.).

The procedure of preparing PCFs involved different stages; first, pine cones were collected from local trees located in Bidezard village close to Shiraz-Iran and then cleaned from dirt and impurities. After that, the scales were cut off from cones and soaked in distilled water for 10 h, at room temperature with a solid content of 10%. Subsequently, wet scales were grinded with coffee grinder (with the model number of FU-341) for 15 min. The primary diluted powder prepared in the last stage was milled with a planetary ball mill for 3 h and the speed of 280 rpm. For this aim, 7 steel balls with 3 different sizes of 6, 10, 16 mm and the total weight of 115 g were used. The mass ratio of powder to balls was 1:20. Chemical (alkali) treatment (mercerization) was the next stage, which was the process of immersion in a solution of 5% sodium hydroxide for 2 h at room temperature. Following that, the powder was treated with water and then centrifuged. This was repeated for 6 times to neutralize the sodium hydroxide. Next, it was dried in the oven for 2 h at 60℃ and eventually screened with the mesh number of 100.

Goat's hair (2-3 mm) used in this research, belonged to the indigenous goats of Semnan Province-Iran. The process of reaching the desirable GHF was simply consisted of cutting the primary hair with scissors, washing it with water, and drying in the oven with the temperature of 60℃ for 3 h.

2-2- Processing of composites

Different PCF composites, GHF composites, and hybrid composites containing both of these reinforcements were made by the following procedures. First, at room temperature the PCFs were dispersed in 18 g acetone by manual mixing and sonication for 15 min. As soon as the dispersion was acceptable, the resin was added to the solution and mixed by manual mixing and sonication for 20 min. It was discovered that in those composites having the GHF as the only or one of the two reinforcements, gradually adding the fibers to resin makes a better dispersion than adding the resin to the whole fibers. Following that, the suspension was put in the vacuum oven for 30 min at 50℃ to evaporate the solvent. Once the solvent was completely evaporated, the suspension was mixed with the hardener by manual mixing. In order to remove voids, the mixture was placed inside the vacuum chamber for 1 h at the room

temperature. Thereafter, the mixture was slowly poured between two metal plates with dimensions of 250×200 mm and left under constant pressure in a way that their distance kept 4 mm, and maintained at this condition for 2 h at room temperature to be cured. To obtain the optimal mechanical properties, the post curing treatment was performed for 1 h at 50℃ + 2 h at 60℃ + 8 h at 80℃. At the end, standard samples for density measurements, mechanical tests, and water absorption evaluations were engraved out of the sheets. For each test 5 samples were prepared and the volume percentage of reinforcements in each sample is available in table 1. For instance, sample RE/1PCF/7GHF is a hybrid composite containing 7% GHF as reinforcement and a composite similar to RE/1PCF as an effective matrix.

2.3. Characterization

2.3.1. Fibers characteristics

The chemical composition (cellulose, lignin, and hemicellulose) of the untreated and chemically treated PCFs was experimentally measured by standard procedures. The determination of cellulose content was performed by using the Krushner and Hoffer's method. Natural detergent fiber method [20] was used to estimate the amount of hemicellulose. Lignin content was measured based on ASTM D-1106-96 instruction.

Tensile properties of GHF were measured using a single fiber tensile tester (model LLY-06A). In order to obtain the mean value, 45 fibers with different gauge lengths of 10, 30, and 50 mm were tested. The test was performed under the conditions of 0.3 cN pretension, and 15 mm/min extension.

2.3.2. SEM

The morphology of the fibers and the microstructure of the composites were characterized using scanning electron microscope (SEM) (two types of instruments were used with the models of VEGA3 TESCAN and CAMBRIDGE S-360). Prior testing, samples were sputter coated with a thin layer of gold (not thick to obscure specimen surface details) in order to prevent charge buildup on specimen surface. Fracture surfaces of samples after flexural and impact testes were also analyzed using SEM.

2.3.3. Mechanical tests

Tensile characteristics of composites were observed using a universal tensile machine Instron 25 at crosshead speed of 5 mm/min according to ASTM D638. Samples geometry and dimensions were selected based on type II of this standard instruction.

Izod impact test is another mechanical test that was implemented to demonstrate the composites toughness, which can define whether the composite is brittle or ductile. To specify the impact test results for composites in this work, samples with dimensions 4×12.7×63.5 mm were prepared following the ASTM D256 standard and tested using a ZWICK machine.

The flexural test with a span of 64 mm was performed as per ASTM D790 standard. Samples with dimensions 4×16×90 mm were cut and a universal flexural machine Instron 25 at a crosshead speed of 5 mm/min was employed. The purpose of this attempt is to provide values for the modulus of elasticity in bending, flexural strength, and deflection at break of the composites.

2.3.4. Density measurement

In order to quantify the void content of samples, both experimental and theoretical densities of samples were obtained. The experimental density was measured using Archimedes method at the room temperature and in water as a medium. The measurement was repeated 5 times for each sample and the average value was reported as the experimental density. In order to examine the theoretical density, it is essential to have the fibers densities. Density measurement of fibers was carried out by using the pycnometer. Toluene as a density known standard liquid was used to perform the density analysis (ρ toluene= 866 kg/m3 at room temperature). Using the following equation, the fibers densities were examined [21]:

$$\rho_{fiber} = \frac{m_2 - m_1}{(m_3 - m_1)(m_4 - m_2)} \rho_{toluene} \quad (1)$$

Where m_1 is the mass of the pycnometer, m_2 is the mass of the pycnometer filled with fibers, m_3 is the mass of the pycnometer filled with toluene, and m_4 is the mass of the pycnometer filled with both fibers and toluene. Theoretical density was calculated based on the formula below:

$$\rho_{theoretical} = \frac{1}{\frac{w_G}{\rho_G} + \frac{w_C}{\rho_C} + \frac{w_r}{\rho_r}} \quad (2)$$

Where w_G, w_C, w_r are weight fractions and ρ_G, ρ_C, ρ_r are densities of GHF, PCF and the resin, respectively.

2.3.5. Water absorption

Water absorption test was conducted to verify the relative rate of water intake by samples when they were immersed. Tests were performed in accordance with D570 ASTM instruction, but it is worth commenting that the test cannot be properly accomplished unless the samples be washed of dirt and be dried in an oven (50℃, 2h). In brief, first 5 samples were provided for each type of composite and then were weighted (W_0). Once they were weighted, they were immersed in a container of distilled water at room temperature, and after 24 h were removed from the water, the wet surfaces were wiped off with a dry and clean cloth, and then were weighted again (W_t). They were immersed again and the same procedure was repeated at the end of the first week and every two weeks until the increase in weight became less than 1% of the total increase (W_i). By using the following equation, water absorption data could be computed:

$$M_t(\%) = \left(\frac{W_i - W_0}{W_0}\right) 100 \quad (3)$$

3. Results and discussion

3.1. Fibers characteristics

3.1.1. PCF characteristics

Table 2 presents the chemical composition of untreated and treated PCFs. It was found that chemical treatment increases the cellulose content and reduces the lignin and hemicellulose contents. At the end of treatment, the cellulose content was increased by 66% and

lignin and hemicellulose contents were decreased by 20% and 67%, respectively. Visual verification of this fact can be observed in Fig1.a and 1.b, which illustrate the SEM images of untreated and treated PCFs, respectively. After evaluation several images, it became clear that the length of the untreated fibers was ranged between 10-25 μm and their diameter from 1 to 3 μm, while the diameter of treated fibers had a range between 0.5-2 μm and the mean aspect ratio was about 15. The reduction in diameter of treated fibers can be explained by the separation of outer epidermis due to chemical treatment. Considering the length of fibers affects the mechanical performance of prepared composite, it is essential that the fibers length be longer than the critical length. According to Cox model, the critical length can be calculated based on the following formula [22]:

$$L_c = 2.3d\left[\frac{E_f(1+\nu_m)}{E_m}\right]^{\frac{1}{2}}\left[Ln(\frac{\pi}{4V_f})^{\frac{1}{2}}\right]^{\frac{1}{2}} \quad (4)$$

Where d is diameter of the fiber, E_f and E_m are the E-modulus of the fiber and the matrix, respectively. ν_m is the Poisson ratio of the matrix and V_f is the volume fraction of the fiber. Calculated values indicate that the length of PCF for all composites is greater than the L_c.

3.1.2. GHF characteristics

The mean values of Young modulus, breaking stress and braking strain of GHF were measured to be 5.8 GPa, 412 MPa and 38%, respectively. The SEM images of GHFs are demonstrated in Fig 2. As it can be seen in Fig 2.a the range of diameter in GHFs is about 20-100 μm with the average of 70 μm. Therefore, the aspect ratio of GHF is about 36. Calculated length of GHFs according to equation 4 confirm that the length of GHF in all composites is much greater than L_c. The surface morphology of GHF is characterized by its scales, which are shown in Fig 2.b in higher magnification.

3.2. Density measurement

The density of the fiber-reinforced composites depends on the fiber density and the amount of fiber in the matrix, thus the combination of PCF and/or GHF with matrix affects the overall density of samples. Fig 3 shows the trend of both theoretical and average experimental densities of all samples. As can be seen, the deviation of theoretical density from experimental density increases with further addition of fibers, meaning that void content becomes greater. Void fraction with addition of fibers is estimated by following equation based on ASTM-D2734:

$$V_c = \frac{\rho_{theoretical} - \rho_{experimental}}{\rho_{theoretical}} \times 100 \quad (5)$$

The values of V_c are represented in Fig 4. The reason of the increase in void fraction is that the structure of composites with higher amount of fibers becomes less compact, implicating that they contain more voids. In addition, the GHF surface topography is liable to make void during the composite preparation.

3.3. Water absorption

Fig 5 shows the changes of water absorbed versus time in different samples. As it can be observed, the water absorption behavior in all samples was almost the same; the rate of water absorbed was high at first and then decreased to the constant value of saturation point. Higher content of fibers was led to a higher amount of water uptake. To elucidate the mechanism of water absorption and its relationship with the behavior of interfaces, we here need to assess the kinetic of water absorption. Fick's theory shows the ability of water molecules to penetrate into the composite structure. According to the Fickian diffusion behavior of samples, for small times when $\frac{M_t}{M_\infty} < 0.5$, the diffusion coefficient can be calculated based on the following formula [23]:

$$D = (\frac{M_t}{M_\infty})^2 \frac{T^2 \pi}{16t} \quad (6)$$

Where T is the thickness of the sample. The values of D can be seen in fig 4, which are in agreement with the experimental results of water absorption. The comparison of D values for composites containing GHF and PCF reveals that the water absorption behavior is much more affected by the GHF than the PCF, even though the void content in their composites is almost the same. This matter can also be seen in fig4 that compares the changes in void content and water absorption with fiber content in different composites. As can be depicted, the water absorption is increased more steeply than void content when GHFs were added to the effective matrix. Although, it was expected that PCF represents a stronger effect on water absorption due to its higher surface area. The reason may be due to the presence of lignin in PCF since lignin is a hydrophobic compound. Another reason could also be the interface of GHF, which is longer than PCF's interface, so this causes creation of extended voids along the interface that leads to a higher amount of water uptake.

3.4. Mechanical properties

3.4.1. Tensile properties

Fig 6 illustrates tensile stress-strain curves of all samples. As it is clear, the tensile strength improved with addition of fibers ranging from 70.1 MPa to 103.3 MPa for ER/3PCF/7GHF that is 25% higher than that of its effective matrix. Also, the same trend is observed in the effective matrix and the highest strength belongs to ER/3PCF, which is 40% higher than the neat sample. The reduction in ductility with increase in reinforcement content can be attributed to the agglomeration of fibers and deviation from the uniform distribution, and consequent stress concentration. However, it is worth mentioning that elongation values at break, which are reported in table 3, are reasonable due to ductile nature of fibers.

To study the effect of reinforcements and their interface behavior on the mechanical performance, the values of tensile modulus were theoretically calculated and then the results were compared with the experimental values. Theoretical tensile modulus of hybrid composites reinforcement were calculated according to the following equation [24]:

$$E_{hyb} = \frac{V_{hyb.PCF}(E_{com.PCF} - (1 - V_{com.PCF})E_m)}{V_{com.PCF}} + \frac{V_{hyb.GHF}(E_{com.GHF} - (1 - V_{com.GHF})E_m)}{V_{com.GHF}} + V_{hyb.m}.E_m \quad (7)$$

Where $E_{com.PCF}$/ $E_{com.GHF}$ is the E-modulus of single fiber composites with the reinforcement volume equal or close to the volume of reinforcements in their corresponding hybrid composites; E_m represents the E-modulus of matrix; $V_{hyb.PCF}$/ $V_{hyb.GHF}$ is the volume filled by the relative reinforcement in hybrid composite; $V_{com.PCF}$/ $V_{com.GHF}$ is the volume occupied by this reinforcement in the single fiber composite; and $V_{hyb.m}$ is the volume occupied by matrix in the hybrid composite. The values of E_{hyb} cannot be calculated unless we know the values E-modulus for single fiber composites. Using the modified Cox model and mixture rule, which is the following equation, the E- modulus of single fiber reinforced composited, can be computed:

$$E_{com.fiber} = E_{fiber}V_{fiber} + E_m(1 - V_m) \quad (8)$$

Where V_m is the volume of matrix. However, to lessen the error, the correlation factor (η) was also designated and the $E_{com.fiber}$ was calculated based on the following equation:

$$E_{com.fiber} = \eta E_{fiber}V_{fiber} + E_m(1 - V_m) \quad (9)$$

For fiber lengths that are long, the term η extends towards unity. Therefore, the model approaches to that predicted from the rule of mixtures for a continuous fiber composite. The value of η was figured using the equation below:

$$\eta = 1 - \left[\frac{tanh\frac{\beta l}{2}}{\frac{\beta l}{2}}\right] \quad (10)$$

Where l is length of fiber and β is a term, which is given below:

$$\beta = \frac{2}{d}\left[\frac{E_m}{E_{fiber}(1+\nu_m)ln(\frac{\pi}{4V_{fiber}})^{\frac{1}{2}}}\right]^{\frac{1}{2}} \quad (11)$$

Where ν_m is the Poisson ratio and d is the fiber diameter [25].

The theoretical and experimental tensile modulus and their proportion in different composites are listed in table 3. The negative values of their proportion indicates that weak performance of interface in load transferring from matrix to reinforcement. Owing to the results in table 3, the proportions in GHF reinforced composites is more negative compared to the effective matrix that is also in agreement with the results of water absorption evaluations.

3.4.2 Flexural Test

Table 4 presents the list of experimental values of flexural strength, modulus, and elongation besides the theoretical values of flexural modulus computed based on the approach described in section 3.4.1. According to tables 3 and 4, the proportions of theoretical modulus and experimental modulus in flexural testing is less negative than their proportions in tensile testing. The reason is that in flexural testing, a variety of concurrent mechanisms occur, including tension, compression, and shear. This justifies why fibers have enhanced flexural performance more than tensile. Addition of fiber fractions has enhanced both flexural strength and modulus. The highest and the lowest flexural strengths belong to samples ER/3PCF/12GHF and ER/1PCF with the values of 207.74 MPa and 126.5 MPa, respectively. The experimental results show that the GHFs have a profound effect on the enhancement of mechanical performance of composites compared to PCFs. This may be due to higher modulus of GHF even though PCF's interface with the resin is better. It is known that fibers with a larger length than the critical length can improve the flexural strength [26]. As it was mentioned before, the length of GHF is much greater than the critical length; this may be another reason why GHFs improved the flexural strength in most composites. In ER/5PCF/12GHF sample the flexural strength decreased by increasing the GHF content due to the higher void content and agglomeration of fibers and stress concentration. As can be seen in table 4, the deflection diminished with increment in the fiber content owing to the stress concentration which is caused by agglomeration of fibers and increasing void content (Fig 4), yet the value of deflection in all samples is high since the fibers are natural with almost a high ductility.

Fig 7 shows the SEM images of fractured flexural surfaces of the composites. The fracture morphology of flexural test performed in this study is generally a combination of four mechanisms: (i) crack formation, (ii) fiber pull out, (iii) fiber fracture, and (iv) void formation. As it can be seen in the figure, the crack formation mechanism usually occurs at the fiber-resin interface and also where the PCFs are agglomerated. In GHF reinforced composites, the weak interface is the main reason for the incident of this mechanism. Sentruk et al [19] also observed that there is a relationship between matrix cracking and interfacial debonding. To explain more, interfacial debonding can cause matrix cracking and inverted. Fig 7.c, 7.e, and 7.f show the fiber pull out mechanism. Generally, the occurrence of this mechanism depends on two parameters: the poor interfacial adhesion between the matrix and the fiber, and the inherent length less than the critical length. The fiber fracture mechanism is also shown in the figure. The GHFs represent a weak interfacial adhesion with the resin, but their inherent length is greater than the critical length. This may be the reason why both pull out and fracture mechanisms of the GHFs were observed. The outer shell of GHF is called the cuticle, which consists of thin overlapping scales that all have a specific orientation. If the load is applied on a contrary direction from the orientation of these scales, the fiber will go through rupture instead of a pull out. This matter is shown in Fig 7.d. As can be seen in this figure, despite the poor interfacial adhesion, the fiber has fractured. Fig 7.c, 7.e, and 7.f illustrate the void formation mechanism, which occurred in high fiber contents.

As mentioned, the interface between the GHF and the resin is weak, which cause not significantly enhancement in mechanical properties of some samples. There are several fiber treatments to improve the fiber-matrix interface that can probably improve the

mechanical properties of GHF reinforced composites as well. Kalia et al [27] reported several popular methods for chemical modification of natural fibers such as mercerization, acetylation, peroxide treatment, and silane treatment. Moreover, Pizzi and co-workers [28] outlined that Corona treatment of fibers improves the tensile and flexural properties of the biocomposites. Also, in an interesting work George et al [29] studied the biological enhancement via fungal and enzymatic treatment of fibers.

3.4.3 Impact test

Fig 8 shows the impact energy of all prepared composites. The impact fracture mechanism is complex since it depends on a variety of interrelated factors, such as fiber fracture, fiber pull out, fiber shear out, fiber length, surface treatments of fibers, and matrix cracking [30]. The lack of stress transfer at the fiber-matrix interface leads to the impact failure. The impact strength of hybrid composites depends on the properties of fibers and on the fiber-matrix interface. Also, it is worth commenting that the impact strength of natural fibers is acceptable and in many cases is even better than synthetic fibers [17]. The influence of GHFs on the impact energy is good and GHF reinforced composites exhibit a high impact energy with the maximum value of 15.1KJ/m^2 for ER/1PCF/7GHF composite. There are two possible explanations for this behavior, (i) the sponge-like structure of GHF that highly damps the energy, and (ii) the pull outed fibers. Also, the impact strength can be even more incremented by reducing the length of GHFs. However, PCFs show a different behavior from GHF and reduce the impact energy. The impact energy of effective matrix diminished by 35% with the addition of 5% PCF, due to the weakening of the uniformity and continuity of matrix via the increase of void percent and stress concentration.

Fig 9 depicts the SEM images of impact fracture surface of composites. Increasing the percentage of PCF improves the adhesion of GHF with the matrix. Visual verification of this matter is shown in Fig 9.b which is a higher magnification of the specified fiber in Fig 9.a. As it can be observed, the fiber shell is peeled off with the resin and macrofibrils are visible, which corroborates the enhancement of adhesion. Fig 9.c shows a GHF's cross-section, which is fractured owing to the orientation of its scales. The picture shows the sponge-like structure of the GHF, that causes the high energy absorption. Fig 9.d demonstrates the brittle fracture surface of ER/5PCF/12GHF composite. Various impact fracture mechanism, such as fiber pull out, fiber fracture, crack formation, and void formation are demonstrated in Fig 9.d, 9.e, and 9.f.

4. Conclusion

In this study, natural fiber hybrid composites with two types of animal and plant fibers were fabricated. After chemical, physical, and mechanical analysis of fibers and composites, the results below were revealed:

1- One of the main problems in most of natural fiber reinforced composites is their high amount of water absorption. But, according to a comparison between the proportion of lignin to cellulose in PCF and other natural fibers we realized that PCF reinforced composites have a much less water uptake due to the higher proportion of lignin to cellulose in PCF.

2- Presence of PCFs caused the enhancement in mechanical properties of composites such as tensile behaviors and flexural behaviors. However, PCF slightly diminished the impact energy. Besides the improvement of mechanical properties in the effective matrix, PCFs have enhanced the GHF-matrix interface bonding.

3- GHFs have improved the mechanical behavior especially flexural strength of composites owing to their special surface topography and reasonable mechanical properties.

4- Despite the impact behavior in other natural fiber reinforced composites, the GHF reinforced composites showed a good impact behavior because of the spongy like structure.

5- As one of the best composites, existence of 1vol.% PCFs in the effective matrix and addition of 7 vol.% GHFs have improved the tensile strength by 61%, flexural strength by 96%, and impact energy by13%. Also, it is possible to attain better performance by using a pretreatment to modify the surface of GHFs.

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Conflict of interest Statement:

The authors declare that there is no conflict of interest.

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Figure Captions:

Figure 1. SEM images of a) untreated PCF, and b) treated PCF.

Figure 2. SEM photographs of a) GHFs, and b) higher magnification of a GHF.

Figure 3. Measured and theoretical values of densities of all samples.

Figure 4. Comparison of water absorption, void contents and diffusion coefficient values trends.

Figure 5. Variation of absorbed water with time for different samples.

Figure 6. Tensile stress-strain curves of different samples.

Figure 7. Secondary detector SEM photographs of fractured surfaces after flexural tests for a) ER/1PCF/7GHF, b) ER/3PCF, c) ER/1PCF/12GHF, d) ER/12GHF, e) ER/3PCF/7GHF, and f) ER/5PCF/12GHF

Figure 8. Measured impact energy of different samples.

Figure 9. Secondary detector SEM images of fractured surfaces after impact tests for a) ER/5PCF/7GHF, b) higher magnification of mentioned area in a, c) ER/3PCF/12GHF, d) ER/5PCF/12GHF, e) ER/7GHF, and f) ER/1PCF.

Tables:

Table 1. Samples coding and proportion of reinforcements in composites (percent by volume).

Code	PCF (Vol. %)	GHF (Vol. %)
Neat ER	0	0
ER/1PCF	1	0
ER/3PCF	3	0
ER/5PCF	5	0
ER/7GHF	0	7
ER/12GHF	0	12
ER/1PCF/7GHF	0.93	7

ER/3PCF/7GHF	2.79	7
ER/5PCF/7GHF	4.65	7
ER/1PCF/12GHF	0.88	12
ER/3PCF/12GHF	2.64	12
ER/5PCF/12GHF	4.4	12

Table 2. Chemical composition of PCF before and after chemical treatment.

PCF fibers	Cellulose content (%)	Lignin content (%)	Hemicellulose Content (%)
Untreated	38.1±2.6	28.2±1.8	29.5±4.1
Chemically treated	63.3±3	22.6±1.6	9.7±3.3

Table 3. Tensile Properties of Samples.

Sample	Experimental Tensile Modulus, GPa	Theoretical Tensile Modulus, GPa	Theoretical/ Experimental Tensile Modulus, %	Tensile Strength, MPa	Elongation at Break, %
Neat	2.95	-	-	59.17	5.5
ER/1PCF	2.97	3.09	- 4.18	70.82	5.7
ER/3PCF	3.11	3.07	1.16	82.50	5.4
ER/5PCF	2.99	3.06	- 2.38	81.67	4.4
ER/7GHF	3.01	3.27	- 8.63	85.76	4.7
ER/1PCF/7GHF	3.18	3.29	- 3.74	95.53	4.8
ER/3PC/7GHF	3.34	3.28	1.94	103.33	4.6
ER/5PCS/7GHF	3.23	3.26	- 0.94	90.83	4.4
12GH	3.13	3.39	- 8.27	88.33	4.1
ER/1PCF/12GHF	3.22	3.43	- 6.77	102.50	3.5
ER/3PCF/12GHF	3.39	3.42	- 0.7	98.33	3.2
ER/5PCF/12GHF	3.24	3.40	- 4.94	90.83	2.6

Table 4. Flexural Properties of Samples.

Sample	Experimental Flexural Modulus, GPa	Theoretical Flexural Modulus, GPa	Theoretical/ Experimental Flexural Modulus, %	Flexural Strength, MPa	Deflection, %
neat	2.60	-	-	98.53	5.9
ER/1PCF	2.93	3.00	- 3.59	126.45	5.7
ER/3PCF	3.02	3.00	0.68	137.79	5.4
ER/5PCF	3.21	3.00	6.42	140.16	3.8
ER/7GHF	3.15	3.23	- 2.59	133.55	5.9
ER/1PCF/7GHF	3.35	3.54	- 5.65	191.77	5.3
ER/3PC/7GHF	3.89	3.54	9.23	204.10	4.9
ER/5PCS/7GHF	3.42	3.54	- 3.60	197.58	4.4
12GH	3.24	3.39	- 4.81	163.35	4.8
ER/1PCF/12GHF	3.98	3.70	7.00	206.19	3.7
ER/3PCF/12GHF	4.32	3.70	14.41	207.74	3.5
ER/5PCF/12GHF	3.54	3.70	- 4.38	191.26	3.2