

Article

Date-Palm-Based Sustainable Hybrid Composite with Cotton and Kevlar Fibre Participation

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Abstract: This research aims to evaluate the physical and mechanical performance of three types of hybrid composites made of date palm (*Phoenix dactylifera* L.) (DP), additional layers of cotton (DP/C) and Kevlar fibres (DP/K). The fibres were formed into flat sheets and employed as reinforcement layers embedded in a polyester matrix. Three-layer and five-layer hybrid composites were created using the hand layup method. The layers have alternative longitudinal–transversal orientation. The composites were investigated for density, thickness swelling (TS), water absorption (WA), flexural strength and modulus of elasticity (MOE) properties. Moreover, the composites were subjected to cycles of water immersion, freezing and drying, and the changes in mass and mechanical performance were analysed before and after the cyclic testing. The hybrid composite with Kevlar as the inner layers displayed better physical and mechanical properties when compared to the other two hybrid composites. A stereo-microscopic investigation revealed that poor adhesion between the layers of composites contributed to a reduction in the mechanical properties of DP/C and DP hybrid composites. The DP/C composite had the highest thickness swelling and water absorption, with the water uptake more pronounced than in the cases of the other composites. The hybridisation of date palms with Kevlar fibres improved the properties of the hybrid composites.

Keywords: hybrid composite; date palm; cotton; Kevlar; polyester resin; cyclic testing; mechanical testing



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1. Introduction

The development of wood composites was driven by the increase in the cost of logs, the promotion of sustainable management of wood raw materials, and market demands [1,2]. There is an increasingly convincing argument for sustainability in the selection process of materials related to the fields of use [2]. Therefore, the increase in demand for sustainable and renewable materials has brought the possibility of using natural fibres in the structure of the composites to the attention of specialists, due to their low cost, light weight, biodegradability and non-hazardous characteristics [3,4]. Natural fibres such as sisal, flax, jute, kenaf, hemp and ramie were employed as reinforcing materials in polymer-based matrices [5–9] to surpass negative impacts on the environment and resource availability issues [10]. Among them, date palm (*Phoenix dactylifera*) (DP) midrib long fibres are possible raw materials for the design and production of lignocellulosic composites.

The date palm is known for its fruits but, from an economic point of view, represents an important source of income for local farmers and the communities where it grows; it also provides the raw material for furnishing, housing and lots of handcrafts [11]. Date palm trees are found in countries like Egypt (1,352,950 metric tons), Saudi Arabia (1,078,300 metric tons), Iran (1,023,130 metric tons), the UAE (775,000 metric tons) and Algeria (710,000 metric tons) [12]. There are more than 120 million date palm trees in the world, and they are distributed in 94 countries [13]. Date palm leaves are considered waste materials, and they are extensively used for the production of natural fibres [14]. Each date palm is pruned, generating

up to 35 kg of biomass per tree, of which the leaves weigh 20 kg [15,16], representing about 4,200,000 tons of natural fibres and an important amount of natural and renewable resources, 20 and 10 times more than hemp and sisal production, respectively, which are commonly used as natural fibres in the structure of composites [17]. With lower cellulose content and lower density than sisal and hemp, date palm fibres provide better wettability resistance compared to the other two natural fibres and contribute to lower-weight composites suitable for automotive and space applications [17]. Date palm fibres can be extracted from the leaves and trunk, and each part's fibres have different properties, which can be modified by applying chemical and physical treatments to control ash, extractive content and surface bonding [18]. The fibre extraction technique is an important factor in obtaining fibres with high-performance properties, and it can be achieved biologically (by retting and enzymatic treatment), chemically (by alkaline treatment, specifically with NaOH) or mechanically (through the decorticator mechanism) [19].

Studies have investigated the possibility of using date palms in the structure of composites. In the literature [11], the improvement of flexural strength properties and bending resistance in concrete and cement with the addition of date palm fibres was reported. Fibres from different parts of the date palm tree with different shapes and sizes were used by researchers to manufacture wood-based composites: trunk and rachis particles were used for the production of particleboard [20]; date palm waste trunk was used for the production of blockboard and battenboard [21]; and date palm pruning residues were used to manufacture MDF [22]. Several research works focused on using this resource in the structure of polymer-reinforced composites. Thus, small fibres with lengths between 1 mm and 1.3 mm and diameters of a maximum of 40 μm were extracted from date palm rachis, trunk and petioles and used to reinforce an HDPE matrix [14]. Short fibres extracted from leaves [23] were used for polyester-reinforced composites, with a bending strength between 28.8 N/mm^2 and 58.1 N/mm^2 . Leaf fibres ground into small particles and mixed with wood flour were used to reinforce polyester, creating a polyester/woven flax fibre sandwich biocomposite matrix [24]. Fibres extracted from date palm stems and polyester resin were used to form treated date palm fibre polyester-reinforced composites in a die with dimensions of 125 mm \times 90 mm \times 20 mm, applying the hand layup method; they were tested for erosion and water absorption and showed severe deterioration of both the matrix and date palm fibres, involving matrix micro-cracking, fibre pulling and fracture [25].

Date palm midribs have also had the attention of researchers. With bending strengths in the range of 80–90 N/mm^2 and compression strengths between 35 N/mm^2 and 42 N/mm^2 , they are close to the mechanical performance of the red European pine [26]. Long textile fibres that could be converted into woven fabrics or nonwoven mats using a combined alkaline/-mechanical treatment were, for the first time, extracted from date palm midribs without testing them as reinforcements for polymer composites [27]. Using date palm midribs and the extraction method mentioned in [27], an oriented, self-bonded mat without chemical or synthetic materials was obtained in the previous research and used to reinforce a hybrid epoxy composite [28]. The present research is a continuation of the investigation on the potential of using these long textile fibres in self-bonded mats as reinforcement in laminate hybrid polyester composites.

The contribution of other natural fibres was also investigated in the laminate structures of date-palm-midrib-reinforced composites, showing that the flexural strength and flexural modulus of elasticity were improved with the contribution of *Calotropis Procera* fibres with low weight and diameters between 0.015 mm and 0.022 mm [28]. A similar natural fibre to be tested in such structures could be cotton. Cotton is a textile fibre obtained from seeds through ginning. Cotton fibres have a matte sheen, and their yellowish-white colour is due to the natural pigments they contain. As a natural fibre, cotton is known for its properties such as low density, good heat conductivity, high flexibility, resilience, elasticity and renewability [29]. Despite the fact that natural fibres are biodegradable, easy to recycle, readily available, and have low density and low cost, their use is limited due to their tendency to absorb moisture, have low adhesion with synthetic components, poor wettability [30] and lack of compatibility

with the matrix [31]. The hybridization of natural fibres with synthetic fibres is necessary to increase their performance, which is difficult to obtain from individual natural fibres [32]. As long as date palm midrib fibres show comparable properties to those of other natural fibres such as sisal, hemp, and flax [27], possible hybrid Kevlar/natural-fibre-reinforced polymer composites can be designed considering the results obtained by other researchers [31]. Kevlar is a strong material, with high rigidity modulus, toughness and thermal stability, belonging to the aramid fibres. It has a wide range of applications, including in aerospace engineering (such as aircraft wing and fuselage structure), bulletproof vests, face shields, ships and body armour [31,33].

The chemical bonding between the matrix and the natural fibres plays an important role in the performance of the composite, with a notable effect on its mechanical properties [34]. Except epoxy resin, which exhibits excellent properties due to its high crosslinking characteristics, adequate strength and dimensional stability [35] and has been often used in the structure of date-palm-reinforced composites [28,36–38], other polymers like polyamide, polyurethane or polyester could be used as matrices in composites with natural fibre reinforcement.

Date palm long fibrillated fibres obtained recently using a combined alkaline–mechanical extraction process of delignification and fibrillation from midribs [27,28] are not sufficiently studied in textile applications, nor as reinforcement for polymer composites. The present study deals with the use of these fibres as reinforcement in polyester composite. The influences of cotton, as a natural and soft fibre, and Kevlar, as a synthetic and strong fibre, were also investigated regarding the bending strength properties, resistance to water and temperature changes in terms of freezing and drying. The results of the present study are oriented towards the finding of an appropriate application of the proposed composites, intended to be used in a humid environment.

2. Materials and Methods

2.1. Materials

2.1.1. Wood Fibres

Date Palm (*Phoenix dactylifera* L.) Fibres (DP)

For the present research, the raw material needed for the extraction of the date palm fibres, was obtained from the date palm groves of Hormozgan province (Rudan city, Iran). The fibres were extracted from the midribs. The midrib is the only part from where the longest fibres can be extracted using the chemical method. The stages of the process for fibre extraction follow the procedure presented by [19,27,28], and they are described in Figure 1.

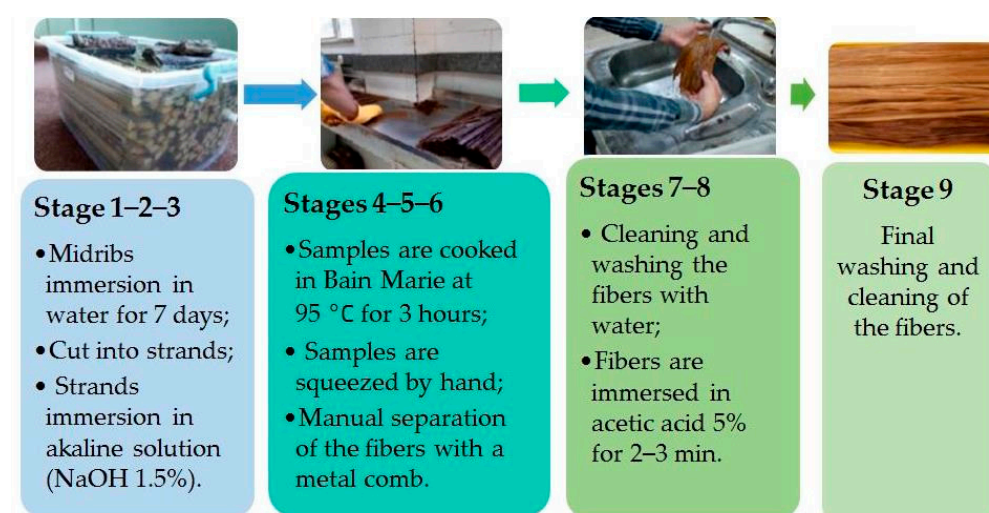


Figure 1. The process of date palm fibre extraction.

The extracted date palm fibres were longitudinally oriented and arranged manually into flat sheets with dimensions of 350 mm × 350 mm (Figure 2a). The measurement made under the stereo-microscope NIKON SMZ 18-LOT2 (Nikon Corporation, Tokyo, Japan) with 240× magnification on a bundle of fibres indicated diameter values between 0.22 mm and 0.37 mm [28].

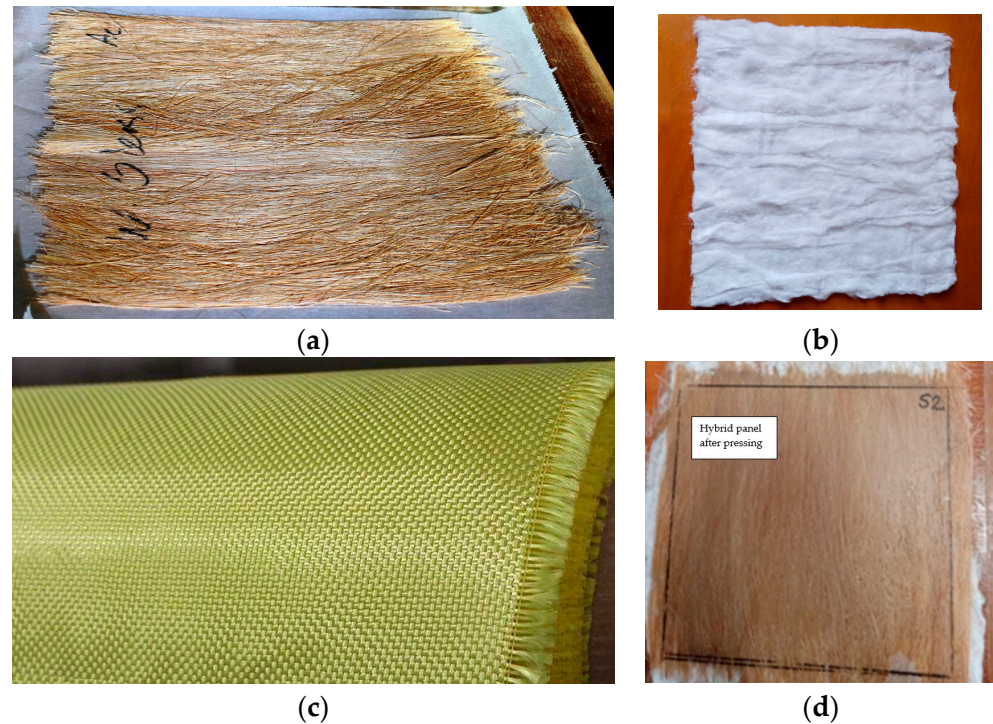


Figure 2. Sheets of reinforcement fibres: (a) date palm; (b) cotton; (c) Kevlar; (d) experimental hybrid composite.

Cotton Fibres

Cotton has a crystalline and fibrillary structure and has the potential to be used in reinforced composites due to its exceptional strength [29]. Cotton wool for medical applications was used in this experiment. The cotton wool was purchased from the Romanian market (Optimum medical, Bucharest, Romania). The cotton fibres were extracted by shredding the wool into a thin mat with a size of 350 mm × 350 mm (Figure 2b). The cotton fibre diameters were measured using the stereo-microscope NIKON SMZ 18-LOT2 (Nikon Corporation, Tokyo, Japan) with 240× magnification and varied between 0.008 mm and 0.02 mm.

Kevlar Fibres

Kevlar is a heat-resistant para-aramid synthetic fibre with a molecular structure of many inter-chain bonds that make it incredibly strong. Kevlar ARAMID fabric VC1 AG170, PLAIN, 170 g/m², width 120 cm, filament around 0.012 mm, and density of 1.44 g/cm³ purchased from the Romanian market (Best Tools company Brasov, Brasov, Romania) and produced by the Vosschemie company (Uetersen, Germany) was used in this research as sheets of 350 mm × 350 mm (Figure 2c). This fabric is bidirectional with 2/2 twill weave. It is suitable for use in polyester, vinyl ester and composite materials: it has low weight, high elasticity and good tensile strength fibre characteristics, making it suitable to be exposed to weather and water. It has the following characteristics: number of threads 6.8 ± 2% threads/cm; tensile strength 3154 N/mm², modulus of elasticity 108,000 N/mm², fabric thickness approx. 0.3 mm; can be processed using the hand lay-up method; recommended to be used for reinforcement polyester, vinyl ester and epoxy resins.

2.2. Composite Design

The date palm/cotton/Kevlar fibre-reinforced polyester hybrid composites were manufactured in laboratory conditions. The two-component polyester resin VISCOVOSS AZUR SUPER+ type was used as the matrix and was purchased from the Romanian market (Best Tools company Brasov, Brasov, Romania). This resin has a density of 1.1 g/cm³ and a viscosity of 900–1100 mPa·s at 20 °C (Brookfield, Toronto, ON, Canada) as specified in the technical sheet. It is an unsaturated, pre-accelerated, ambient-temperature-curing polyester resin with low styrene emissions. Methyl ethyl ketone peroxide (MEKP) was used as the hardener and was added to the base component resin with a participation rate of 3% of the resin weight.

Natural fibres (DP and C) and synthetic fibres (K) were used to reinforce the polyester matrix and to manufacture the hybrid composites. The design of the three types of composites is presented in Table 1.

Table 1. The design of experimental hybrid composites.

Code	Structure	Design ¹	Date Palm Fibres Weight Fraction (%)	Cotton/Kevlar Fibres Weight Fraction (%)
Date palm (DP)	3 layers (DP-DP-DP)	Alternating parallel–perpendicular orientation of layers	20	-
Date palm/cotton (DP/C)	5 layers (DP-C-DP-C-DP)	Alternating parallel–perpendicular orientation of layers	17	2.17
Date palm/Kevlar (DP/K)	5 layers (DP-K-DP-K-DP)	Alternating parallel–perpendicular orientation of layers	15.6	7.35

¹ The layers for the faces were oriented longitudinally in each structure.

Each layer of the composites was firstly weighed with an accuracy of 0.01 g, and the sheets with similar weight were used for the faces in the composite structures. The average weight of the layers was as follows: the DP layers had 33.26 g for the faces and 36.81 g for the core; the cotton layers had 6.6 g; and the Kevlar layers had 24.35 g. The proportion of the fibres in the polyester resin matrix was 20 wt% for DP, 19.17 wt% for DP/C and 22.95 wt% for DP/K (Table 1). The proportion of the cotton and Kevlar fibres from the total volume of the panels is cotton fibres 9.76 vol% for DP/C and Kevlar fibres 8.18 vol% for DP/K.

The polyester resin amount was calculated by multiplying the weight of each layer as follows: five times for the date palm fibres, seven times for the cotton fibres and three times for the Kevlar fibres. These rates were established according to the recommendations of the manufacturer for the synthetic fibres and after preliminary determinations for the date palm fibres and natural fibres similar to cotton [28]. The resin was applied via brush on each individual sheet of fibres. The working temperature was about 24 °C, and the working time for applying the resin was up to 30 min to avoid the stickiness effect as recommended in the technical sheet. On the top and bottom of the sandwich hybrid composite, white silicon baking paper was used to avoid sticking to the support where the sandwich was formed (Figure 2d). Each of the laminate composites was placed between two blockboard panels, and a weight of 20 kg was used for cold pressing the composites at a pressure of 0.019 bar for three days. Fully curing this resin needs at least 48 h, according to its technical sheet. The amounts of resin were, as follows: 490 g (DP structure), 595 g (DP/C structure), 660 g (DP/K structure). The method applied to manufacture the experimental hybrid composites is presented in Figure 3.

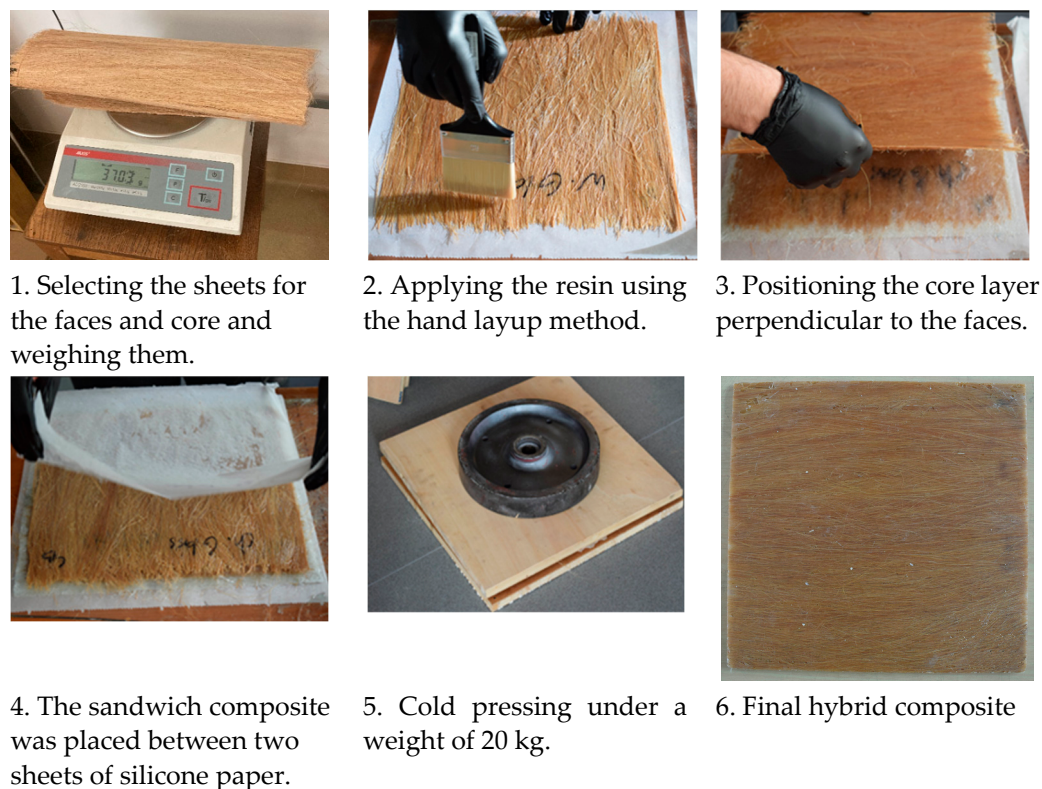


Figure 3. The manufacturing process of the hybrid composites.

Three replicates of each hybrid composite type (DP, DP/C, DP/K) were manufactured. After six days of conditioning at 23 °C and 65% relative humidity of the air, the experimental panels were sized at 300 mm × 300 mm. The test specimens were cut according to the specific standard requirements for the evaluation of the physical properties, such as density, moisture content, thickness swelling (TS), water absorption (WA) and mechanical properties related to flexural strength (MOR) and modulus of elasticity (MOE).

2.3. Testing

The density was determined according to EN 323:1996 [39], the moisture content according to EN 322:1996 [40], and the thickness swelling (TS) and water absorption (WA) according to EN 317:1996 [41], with specimens with dimensions of 50 mm × 50 mm (length × width). The samples were immersed in distilled water at a temperature of 20 °C for 24 h. The thickness and the mass of the samples were recorded before and after immersion in water at 2, 24, 48, 72, 96, 120, 144, 168, 192 and 216 h. An electronic calliper with an accuracy of 0.01 mm and the electronic scale with the accuracy of 0.01 g were used to measure the thickness and to weigh the samples. The purpose of this test was to assess the water resistance and the dimensional stability of the hybrid composites. The flexural strength (MOR) and modulus of elasticity (MOE) were evaluated according to EN 310:1996 [42], the tests being carried out with the help of a Zwick/Roell Z010 universal testing machine (Ulm, Germany). Six samples were used for each type of hybrid composites and each test.

The hybrid structures were designed to resist the humid environment. Thus, in addition to the water immersion test, they were also subjected to cyclic moisture resistance tests according to EN 321:2003 [43]. The experimental panels of 300 mm × 300 mm were subjected to three exposure cycles consisting of immersion in water followed by freezing and then drying at a high temperature. After cyclic testing, their thickness, mass, MOR and MOE were measured.

A water bath at a temperature of 20 ± 1 °C was used for the water immersion of panels in the first cycle for 24 h. The other two cycles were carried out in a test chamber of HL type [DongGuan City, China] set to the 24 h freezing cycle at temperatures between -12 °C and -25 °C and drying for 72 h at 70 ± 2 °C. Three cycles were performed per edge of each composite. After completing these cycles, the panels were conditioned at 23 °C and 65% relative humidity of air until constant mass. The changes in thickness, mass and flexural properties were tested and compared to those obtained before cyclic testing. The increase in thickness (dT) and the mass decrease (dM) of panels after cyclic testing were calculated with the following equations:

$$dT = \frac{t_f - t_i}{t_i} \times 100 \quad (1)$$

where

t_f —the final thickness after cyclic testing, in mm;
 t_i —the initial thickness before cyclic testing, in mm.

$$dM = \frac{M_f - M_i}{M_i} \times 100 \quad (2)$$

where

M_f —the final mass after cyclic testing, in g;
 M_i —the initial mass before cyclic testing, in g.

A microscope investigation of the samples before and after cyclic testing was carried out using a NIKON SMZ 18-LOT2 (Nikon Corporation, Tokyo, Japan) stereo-microscope. This allowed for a better visualization of the structures and of the adhesion between the component layers. The microscopic analysis was made on the cross sections of the experimental hybrid composites with $30\times$ magnification. Six samples from each experimental composite, were prepared to perform the test.

2.4. Statistical Analysis

The values of the physical properties (density, TS, WA) and mechanical properties (MOR and MOE, before and after cyclic testing) were compared individually. A single-factor analysis of variance (ANOVA) was performed with Minitab Statistical Software Version 21.1.0 at a 95% confidence level and a significance level of 0.05 ($p < 0.05$). The analysis shows how the properties of the hybrid composites were affected by the presence of cotton and Kevlar in the structure. Furthermore, Tukey's test was utilized to specify the significant differences created by the fibres.

3. Results and Discussion

3.1. Density and Moisture Content

The density and the moisture content of the experimental hybrid composites are presented in Figure 4.

The highest density value was obtained for the panels with date palm fibres (1012 kg/m^3) due to the fact that the quantity of resin applied was about 30% greater than the resin amount applied on the layers of the other two composites. The density of composites was not influenced by the densities of the fibres, which were almost in the same range of values: 1.44 g/cm^3 for Kevlar fibres, between 0.9 g/cm^3 and 1.2 g/cm^3 for date palm fibres and 1.5 g/cm^3 for cotton fibres [17]. The density of DP with polyester was about 44% lower than similar composites with epoxy resin as the matrix [44]. Both resins are generally used as matrices for natural fibre composites that cure at environmental temperatures. The lower density of the hybrid composites with polyester could be an advantage in applications where lightness is essential, such as in aerospace and automotive applications.

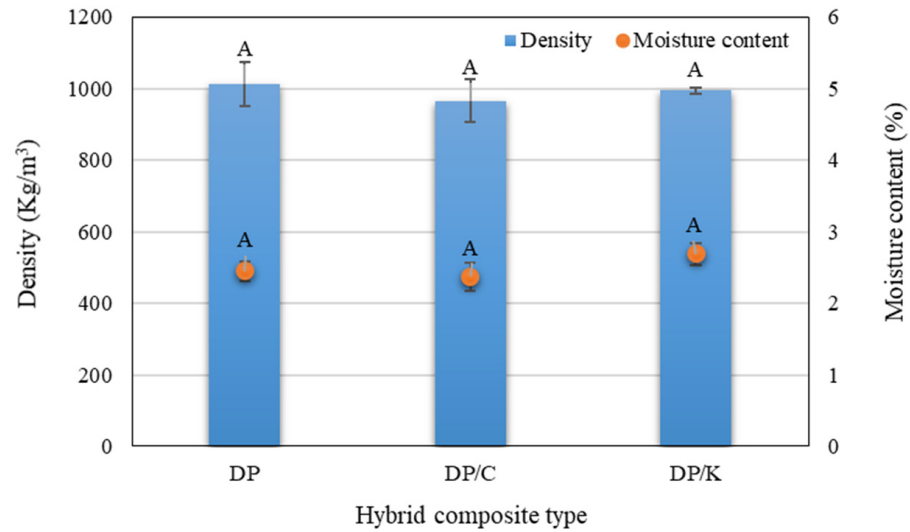


Figure 4. Density and moisture content (average values) (A—variables with the same letter mean that the difference is not statistically significant).

Furthermore, there were no big differences between the moisture content values, these being similar to those found in the literature [45].

According to the statistical examination, the investigation revealed the absence of statistically significant distinctions in both density and moisture content values across all three types of hybrid composites, with findings established at a 95% confidence level. The computed *p*-values and F-values for density and moisture content were 0.354, 0.182, 1.17 and 1.97, respectively. Additionally, the outcomes derived from the Tukey test corroborated with the aforementioned findings, categorizing all three variants of hybrid composites into identical groups concerning both density and moisture content.

3.2. Thickness Swelling (TS) and Water Absorption (WA)

The values obtained for TS and WA during the period of 216 h (9 days) of immersion in water are presented in Figures 5 and 6. By analysing the thickness swelling values, it can be seen that after 24 h and 216 h, the lowest values were obtained for the composites with Kevlar (1.22% and 2.3%, respectively) followed by those with cotton (1.01% and 3.0%, respectively) and date palm fibres (2.74% 5.42%, respectively) (Figure 5).

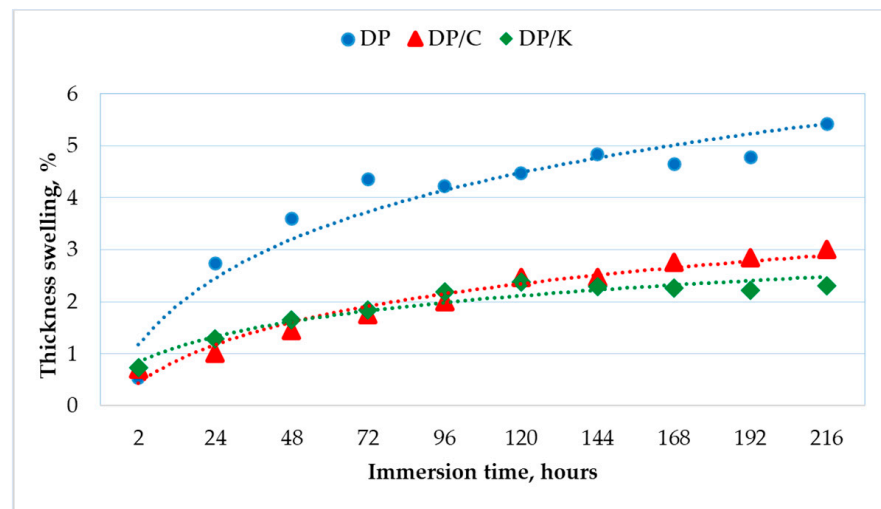


Figure 5. The dynamics of swelling in thickness for the 3 structures (DP, DP/C and DP/K).

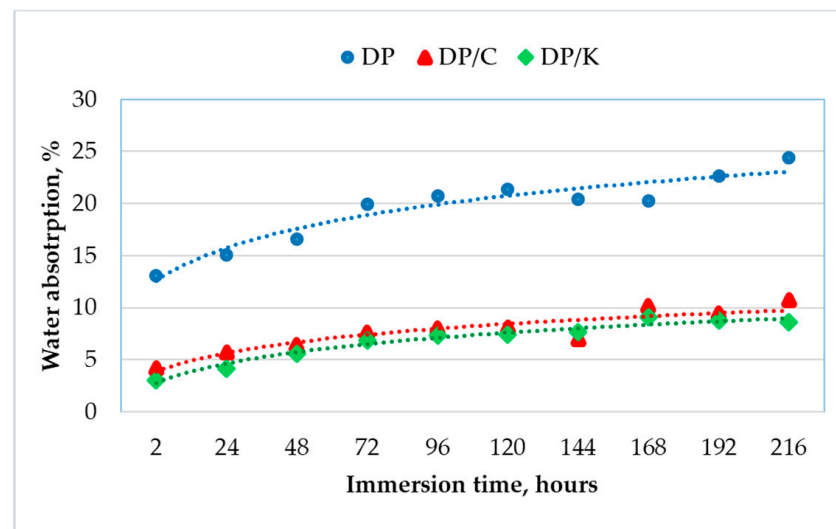


Figure 6. The dynamics of water absorption for the 3 structures (DP, DP/C and DP/K).

In the first 24 h, the thickness increased at about 0.02%/hour for the composites DP/C and DP/K and at about 0.09%/hour for DP. These results can be explained by the sensitivity of date palm fibres to water absorption due to their hydrophilic character, as was also observed by [46]. Another cause may be related to the presence of voids and pores in the structure, due to uneven application of the adhesive on the surfaces of the layers.

For all composites, the water uptake increased more rapidly in the first 72 h; then, until the end of the period, the dynamic of the water uptake decreased. This is in agreement with [47,48] (Figure 6).

The rate of swelling and absorption was more pronounced for the DP composite compared to the other two. The presence of high voids in DP specimens increased the water absorption, as water was trapped in the voids. After 24 h and 216 h, the water absorptions were 15% and 24.3%, respectively, for DP; 5.6% and 10.8%, respectively, for DP/C; and only 4.2% and 8.6%, respectively, for DP/K. Reinforcement with Kevlar fibres improved the performance in terms of water uptake by 20% compared to DP/C and by about 60% compared to DP.

However, the addition of the cotton and Kevlar fibres in the structure of the hybrid composite significantly ($p < 0.05$) affected both TA and WA after 24 h ($p < 0.01$) and 216 h, for which this influence was more evident, since $p < 0.009$. This explains the better interface between polyester resin with cotton and Kevlar fibres.

In Table 2, the equations that describe the dynamic of thickness swelling and water absorption during the period of testing are presented. The variation in TS and WA over time is expressed by a logarithmic curve with a high correlation factor ($R^2 > 0.9$).

Table 2. Equations describing the dynamics of TS and WA.

Code	TS	WA
DP	$y = 1.8459\ln(x) + 1.1636$ $R^2 = 0.9226$	$y = 4.5477\ln(x) + 12.594$ $R^2 = 0.911$
DP/C	$y = 1.067\ln(x) + 0.4358$ $R^2 = 0.9608$	$y = 2.5452\ln(x) + 3.8948$ $R^2 = 0.8393$
DP/K	$y = 0.751\ln(x) + 0.7491$ $R^2 = 0.9186$	$y = 2.6858\ln(x) + 2.7968$ $R^2 = 0.9659$

The natural fibres' cell walls contain free hydroxyl (OH) groups, which are a favourable medium for water absorption, leading to the swelling of fibres within the matrix. As a consequence, the interfacial adhesion between the matrix and fibres can be destroyed and voids

or cracks can occur, negatively influencing the mechanical properties and performance of the composites [49,50].

These disadvantages of natural fibres can be reduced or removed by hybridization with synthetic fibres, as in this case with Kevlar, which led to higher resistance to moisture and better aging properties.

3.3. Resistance to Moisture

The test of resistance to moisture revealed the performance of the hybrid composites when exposed to different climatic conditions. The changes in thickness, mass and mechanical properties were analysed. At the end of the cycles (water immersion, freezing and drying), no visible changes were observed on the surfaces of the specimens; however, a slight increase in thickness (dT) of all composites was found, more obviously so for DP/C, at about 6%, compared to 4.8% for DP and 4% for DP/K (Figure 7).

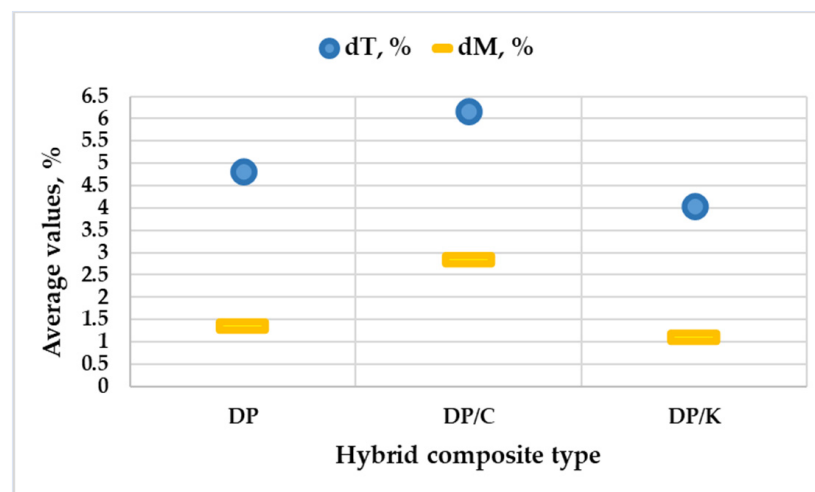


Figure 7. The differences in thickness (dT) and mass (dM) after cyclic testing.

A slight decrease in mass of the composites (dM) was noticed, in the range of 1–2.8% (Figure 7). Similar findings were reported by [51] for hybrid composites made with kenaf and glass fibres after freeze-drying exposure.

The increase in thickness was caused mainly by the hydrophilic character of natural fibres due to the presence of hemicellulose [52] and, in terms of other factors, by the small voids produced inside of structures because of the poor impregnation of date palm fibres into the polyester resin compared to the Kevlar composite (DP/K). Tensile forces can occur during freezing-drying in the polymer matrix, due to the expanding fibre volume in the saturated state after water immersion. These lead to some micro-cracks or voids in the structure (Figure 8d). These voids are more evident in the composites DP/C and DP which had greater decreases in mass compared to the DP/K structure.

DP/C and DP registered decreases in mechanical properties after cyclic testing of about 25% and 6.5%, respectively, for MOE and of about 13% and 5.8%, respectively, for MOR compared to the values obtained before testing. The substantial strength losses occurred in the composite structures, induced by degradation through freeze-drying mechanisms, which cause losses in bonding at the fibre–matrix interface and via the micro-cracks produced by internal stresses [46,51,53]. DP/K performed better, Kevlar fibre being slightly stronger at low temperatures.

After cyclic testing, the flexural strength and modulus of elasticity of DP/K registered slight decreases of about 1.4% and 2%, respectively (Figures 7 and 8).

In the literature [54,55], the effect of a freeze–thaw environment has been studied on carbon-fibre- or glass-fibre-reinforced polymer composites, reporting insignificant effects on shear, axial and flexural properties.

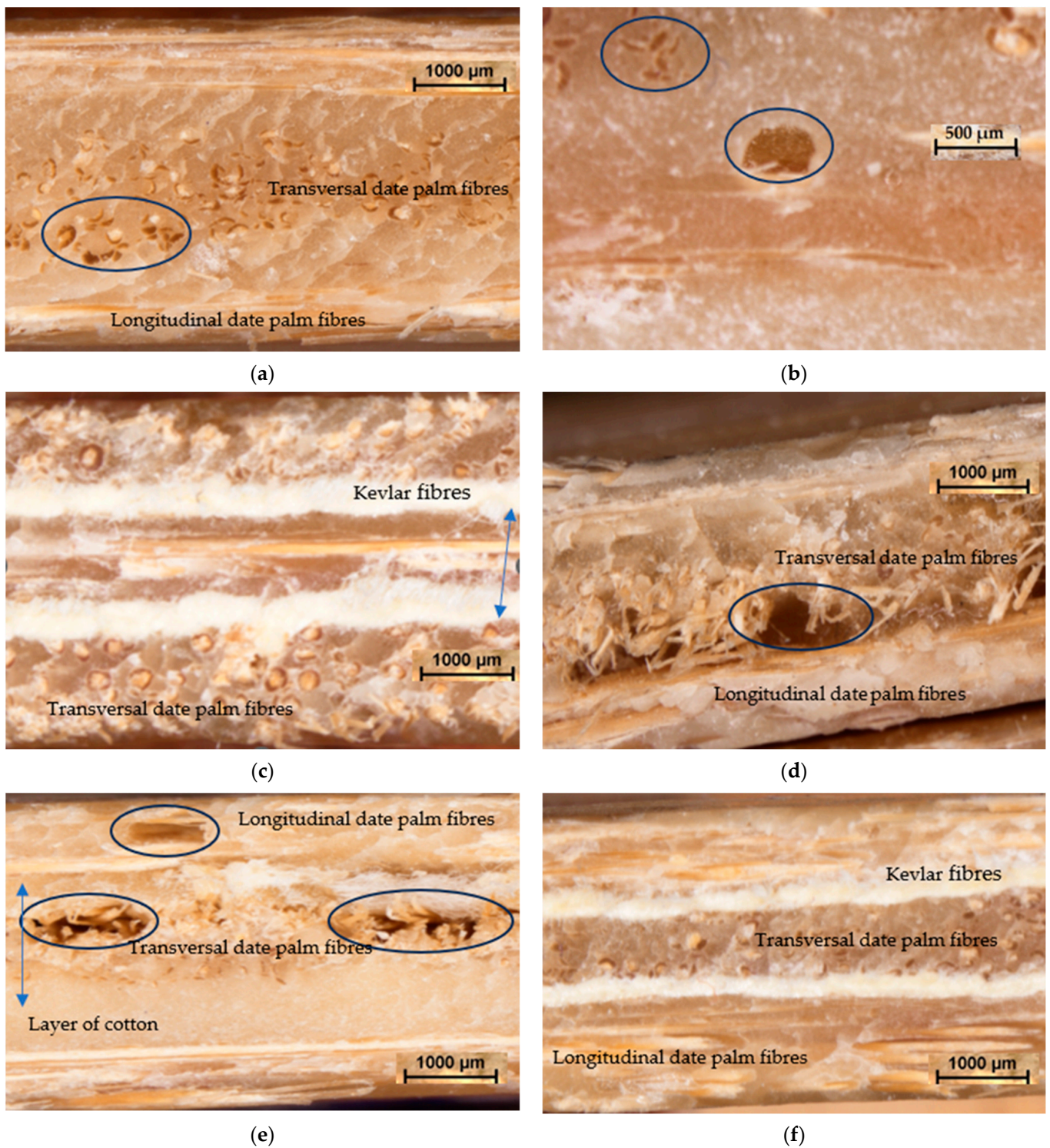


Figure 8. The microscopic investigation of the hybrid composites' structures: (a) DP before cyclic testing; (b) DP/C: detail in the cotton layer before cyclic testing (60× magnification); (c) DP/K: compact structure before cyclic testing; (d) DP after cyclic testing; (e) DP/C after cyclic testing; (f) DP/K after cyclic testing. The circled areas represent the voids inside structures.

3.4. Microscopic Investigation

A microscopic analysis was made on cross-sections of the hybrid composites before and after cyclic testing (CT). Some small voids in the date palm middle layer (cross-section) (Figure 8a) and in the cotton layer (Figure 8b) in the structure DP/C can be seen before the

cyclic testing. These influenced negatively the behaviour of the structures, decreasing their resistance to water. The impregnation with resin of the cotton layers was difficult and as a consequence, after cyclic testing, voids occurred in some areas in the vicinity of the date palm fibres, as can be seen in Figure 8e.

Larger voids were observed also in a few DP specimens at the interface area located between date palm fibres and the polyester resin matrix after CT. This is due to the poor wettability between the fibres and the matrix, leading to insufficient impregnation. This non-continuity in the structure caused a decrease in strength after CT, as can be observed in Figures 9 and 10. This phenomenon was observed also by [56] after freeze-thaw exposure, which induced deterioration of natural fibre composites.

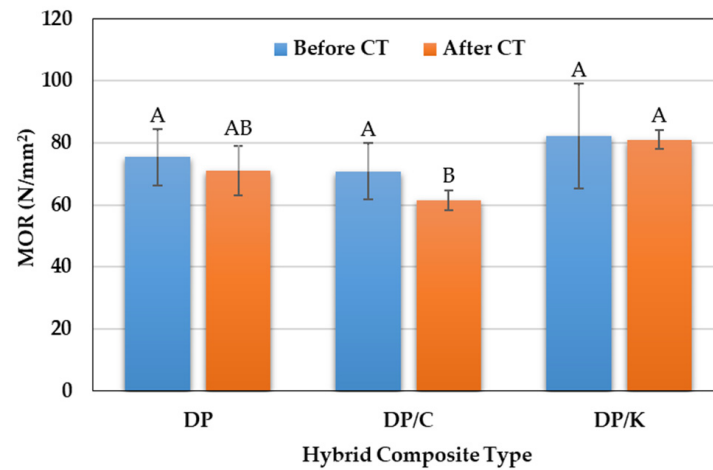


Figure 9. Comparative values of MOR for the 3 structures before and after exposure to cyclic testing (CT) (variables with the same letter mean that the difference is not statistically significant and those with different letters are statistically significant).

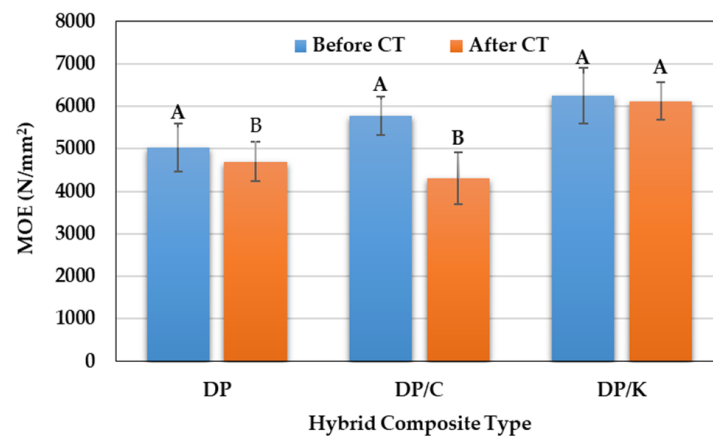


Figure 10. Comparative values of MOE for the 3 structures before and after exposure to cyclic testing (CT) (variables with the same letter mean that the difference is not statistically significant and those with different letters are statistically significant).

3.5. Mechanical Properties

In Figures 9 and 10 are presented the flexural strength (MOR) and modulus of elasticity (MOE) values before and after cyclic testing.

The DP/K hybrid composite exhibited the highest values of flexural strength and modulus of elasticity: 82.24 N/mm² and 6248 N/mm², respectively. Similar results were found by [30], who also confirmed that hybrid composites with Kevlar show higher mechanical properties.

Lower values of MOR and MOE were achieved for DP/C and DP composites, the values ranging between 70.78 N/mm² and 75.4 N/mm² and between 5774 N/mm² and 5028 N/mm², respectively. The natural fibre composites exhibit inferior mechanical properties compared to synthetic fibres, and in the hybrid composites, these properties mainly depend on the binding ability between the matrix and the fibres [57]. DP/C had the lowest density and the adhesive amount applied to each layer was about 40% lower than that applied to DP; consequently, the flexural strength decreased by 14% compared to DP. The cotton fibres did not improve the strength performance of the hybrid composite, due to weaker fibre–matrix interfacial bonding. After cyclic testing, the mechanical properties were analysed and no substantial changing was observed in the case of DP/K. The resin was much easier to apply to the Kevlar sheets and the resin amount was greater than in the case of DP/C. The resin penetrated better in all layers and no voids were observed in the structure (Figure 8f). In the case of the other two composites (DP and DP/C), when subjected to water immersion (first cycle), the softening of fibres occurred, as hydroxyl groups contained in date palm and cotton absorbed water. Then, the expansion of water molecules and contraction of the polymer matrix happened in the freeze cycle, leading to the degradation of the bonding between the fibres and the matrix, further influencing the mechanical properties. DP/C registered a decrease in MOR and MOE by 24% and 30%, respectively, and DP registered decreases by 12% and 23%, respectively, compared to the DP/K composite.

The flexural strength (MOR) and modulus of elasticity (MOE) before cyclic testing were not influenced by cotton and Kevlar fibres in the structures, as a statistical analysis displays no significant effect ($p < (0.2-0.6)$). However, after the cyclic test, the thickness swelling, MOR and MOE were statistically significantly affected by Kevlar layers ($p < (0.01-0.004)$), whereas cotton layers had no significant effect on MOR and MOE after cyclic testing ($p < (0.1-0.4)$). This demonstrates a better interface between polyester and Kevlar fibres compared to cotton fibre, the behaviour of which is influenced by its hydrophilic properties.

Due to their low density and good performance in the freeze-dry test, the experimental hybrid composites with Kevlar (DP/K) could be alternative materials for metal, which in the marine condition is susceptible to corrosion and cracks in time. On the other hand, due to their high flexural strength (75–82 N/mm²) and minimal changes in thickness after water immersion for 216 h and cyclic testing (between 2.3% and 4%), structures DP/K is more reliable for application in construction for floors or roof tiles where moisture resistance is required. However, related to future requirements for sustainable resources and low-impact products, the combination of natural fibres in a hybrid product like DP/C could be an effective solution for indoor partition panels or floor tiles where high flexural strength of date palm fibres with the good impact properties of cotton fibres could be combined.

Durability is an important issue for hybrid composites; thus, further research needs to be carried out to improve the interfacial bonding between fibres and the matrix to increase the mechanical properties and the performance with regard to moisture, considering that natural fibres can replace synthetic fibres in a wide range of outdoor applications.

4. Conclusions

Oriented self-bonded mats of date palm long fibrillated fibres extracted from midribs are very suitable as reinforcement for polyester composites in the form of laminates, proving to have a good adhesion with polyester resin.

The positive influence of the two additional layers of cotton and Kevlar mats in the structure was noticed in a decrease in water absorption and thickness swelling.

The cyclic test consisting of immersion into water, freezing and drying negatively affected the initial mechanical properties of the composites, especially for the structures with two additional layers of cotton, and less affected the structures with Kevlar mats.

The cracks and voids revealed by the microscopic investigation on the DP and DP/C structures after the cyclic test do not recommend these structures to be used in very humid

climates with alternating positive and negative temperatures. Instead, the participation of Kevlar mats in the laminate structure of the date-palm-reinforced polyester composite brings advantages of higher resistance to water and improved mechanical performance, even after immersion in water and being subjected to abrupt differences in temperature. For this reason, the hybrid composite with Kevlar fibres (DP/K) exhibits promising characteristics to be recommended for outdoor applications, in the marine environment, and also in the construction of floors or roof tiles, where moisture resistance is required.

Further studies are envisaged to evaluate other properties such as impact resistance, behaviour in salt water, and the addition of other natural fibres in order to improve the performance of date-palm-based sustainable hybrid composites. Further research on the economic feasibility of these composites will be made so as to create a comprehensive picture of the acceptability of their use.

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