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jmr&t
Journal of Materials Research and Technology
journal homepage: www.elsevier.com/locate/jmrt



Original Article

A novel approach to design sustainable fiber reinforced materials from renewable sources: mathematical modeling for the evaluation of the effect of fiber content on biocomposite properties



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ARTICLE INFO

Article history:

Received 11 November 2020

Accepted 3 March 2021

Available online 9 March 2021

Keywords:

Biocomposites

Natural fibres

Natural fibre composites

Mechanical properties

Transport properties

ABSTRACT

The paper reports a sustainable, fast and efficient methodology to treat natural hemp fibers (HF) using a mechanochemical approach. Mechanical milling was used to carry out an alkaline attack on HFs for 30 min at ambient temperature. Composites HF/pectins were prepared by varying the fiber weight fraction (3%; 7.5%; 10%; 20% w/w by weight). The improvement in thermal degradation, mechanical and barrier properties to water vapor was correlated with the fiber volume fraction and mainly due to the improved fiber-matrix adhesion. The fibers–matrix interaction was then evaluated by analyzing and modeling the mechanical properties using several mathematical models: a modified Nielsen and Pukánszky and Smith models. Sorption isotherms to water vapor were analyzed through a modified Guggenheim, Anderson, de Boer (GAB) model where a new parameter, α , was introduced to consider the heterogeneity of the system. Finally, a modified Burgezman model was used to fit the experimental data and support the improvement in water diffusion with fiber loading.

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1. Introduction

The design and the preparation of composite materials made of renewable and sustainable resources has become one of the greatest challenge of materials science and technology. Their production and utilization are driven by several factors such as sustainable growth, lower carbon footprint, energy security and effective resource management, while structural and functional properties of the materials are simultaneously

improved. The lack of fundamental knowledge in the processing of the raw materials to produce composites from renewable sources is still a great limitation for their production and applications. Natural fibers from plants are receiving great attention from the academic research as well as from the industrial world since their potentiality as fillers in polymer composites for their environmentally friendly nature and sustainability [1–3]. The natural fibers, as reinforcement in composites, are environmentally friendly material which

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possess some interesting properties such as economicity and lightness. In the last years, hemp fibers (*Cannabis sativa*) are gaining a wide interest, since they can be used as composite materials reinforcement, bio-absorbent for water remediation, clothing manufactures, carbon fiber precursors [4–6]. The chemical composition of hemp fibers is very complex, being based of cellulosic and non-cellulosic constituents. Non-cellulosic components are hemicelluloses, pectin, lignin, fat and waxes and water-soluble substances, whereby hemicellulose, lignin and cellulose are the main components that significantly affect composite properties [7,8]. The key factor to obtain biocomposites with improved physical properties for specific end-use applications concerns a good fiber-matrix adhesion, to tackle the biofiber drawbacks and to improve compatibility with the matrix. As far as natural fiber concerns, it is fundamental to remove external non cellulosic materials, and expose the crystalline inner cellulosic component, because it is known that cellulose content and morphology influence the physical, thermal, mechanical, and chemical properties of hemp fibers [9]. The most common chemical treatment refers to the alkaline attack (mercerization) that is able to remove the non-cellulosic constituents [10,11]. Such treatment often requires temperatures up to 120 °C [12] or long treatment times up to 48 h [13]. Mechanochemistry represents an interesting and alternative tool to perform chemical reactions and materials modifications by application of mechanical energy. By using the appropriate processing conditions, it is possible to drastically reduce the time of processing and work at ambient temperature. In a previous work, we reported the use of mechanochemical treatment to modify natural hemp fibers in alkaline conditions at ambient temperature and for different processing times (i.e., 30 min, 1 h, 4 h, 7 h) [14]; such treated fibers were used as fillers at 3% w/w in a pectin matrix. Thermal degradation behavior, mechanical and barrier properties (sorption, diffusion, and permeability) to water vapor were evaluated and compared to unfilled pectin and pectin loaded with raw HFs. A further study was then carried out by analyzing the effect of fiber weight fraction (3%; 7.5%; 10%; 20% w/w) on bio-composite performances. Thermal, mechanical and barrier properties were evaluated and compared with unfilled pectin matrix. In particular, the evaluation of barrier properties is crucial because a high moisture content affects dramatically the physical and chemical ageing of the composites and, thus, their lifetime in interactive environments. The knowledge of the contribution of the thermodynamic parameter (sorption) and the kinetic parameter (diffusion) might help to design the composites for targeted applications. Finally the experimental results were fitted using various mathematical models.

2. Materials and methods

2.1. Materials

Hemp fibers (HF) were supplied by Nafco Italia SRL Company. NaOH (Cas Number: 1310-73-2) in pellet form was purchased from Sigma Aldrich. Pectins from apple with molecular weight 30,000–100,000 Da and a degree of esterification about 70–75%, on a dry basis, total impurities $\leq 10\%$ water (CAS

Number: 9000-69-5) were purchased from Sigma Aldrich in powder form. All materials were used as received.

2.2. Methods

Thermogravimetric analyses (TGA) were carried out in an air atmosphere with a Mettler TC-10 thermobalance from 30 °C to 800 °C at a heating rate of 10 °C/min.

Mechanical properties of the samples were evaluated, in tensile mode, at room temperature using a dynamometric apparatus INSTRON 4301. Experiments were conducted at room temperature on pectin and composites' films with the deformation rate of 5 mm/min. Elastic modulus was evaluated in the deformation range of 0.1%. Data were averaged on five samples.

Barrier properties of water vapor were evaluated through a DVS automated multi-vapor gravimetric sorption analyzer, using dry nitrogen as a carrier gas. The temperature was fixed to 30 °C. Samples were exposed to increasing water vapor pressures obtaining different water activities $a_w = P/P_0$ (from $a_w = 0.1$ to $a_w = 0.8$), where P is the partial pressure into the gravimetric chamber, and P_0 is the saturation water pressure at the experimental temperature. The adsorbed water mass was measured by a microbalance and recorded as a function of time. From the sorption kinetics, it was possible to derive the diffusion coefficient at each activity.

2.3. Biocomposites preparation

Raw hemp fibers (HF) were treated following a reported procedure [14]. Raw hemp fibers (HF) were firstly soaked in liquid nitrogen for 3 h. Then, the frozen fibers were cut using a grinder. The exposition to cryogenic temperature leads to develop residual thermal stress, which induces the generation of forces that contribute to the destruction of the fiber–gum interface. Being it weak, the applied external load generates a crack that extends up to debonding the interface between the brittle gum and the ductile fibers [15]. The ground fibers were then treated with an alkaline solution (HF/NaOH = 1:1 w/w) fixing a liquor ratio equal to 1:20 through a mechanochemical functionalization employing a high energy ball milling (HEBM-Retsch-PM 100) using five zirconium oxide spheres as grinding medium. The milling times was 30 min. The treated fibers were then washed with distilled water until pH = 7 was reached and placed in a vacuum oven at 40 °C for 8 h. Biocomposites obtained from natural pectin from apple were prepared, solubilizing 1 g pectin in 30 mL of distilled water. It was then added glycerol as plasticizer (3% v/v). The solution was stirred at 80 °C for 1.5 h. After completely solubilizing the pectin powder, hemp fibers at different percentages (3 %w/w; 7.5 %w/w; 10 %w/w; 20 %w/w by weight), mechanochemically modified, were added and the solution was submitted to ball milling at room temperature for 1 h in a Retsch (Germany) planetary ball mill (model PM 100), using a cylindrical steel jar of 50 cm³ with 5 zirconium dioxide balls of 10 mm of diameter. The rotation speed used was 450 rpm. The mixtures obtained were poured in Petri dishes and slowly evaporated. Film of pure pectin and pectin filled with raw HF was also prepared in the same described experimental conditions.

3. Results and discussion

3.1. Thermogravimetric analysis

Fig. 1 shows the thermogravimetric curves of the neat pectin and pectin/hemp fibers biocomposites. It is known that the incorporation of fibers as reinforcement in composites could involve changes on the thermal properties of the resulting materials [16].

The degradation of pectin could be considered a sequence of complex phenomena in which two main thermal steps could be evidenced: loss of water and pyrolytic decomposition of primary and secondary decarboxylation involving the methoxy groups and carbon in the ring [17]. The fibers increase the thermal stability of the biocomposites and such improvement is a function of filler loading (from 95 °C to 147 °C for pure pectin and pectin/HF 20% at 95%). Compared to the neat pectin, highly hydrophilic, the presence of hemp fibers could lead to a decrease in OH groups availability which might be involved in weak interaction with polar groups of pectin matrix. As a result, the water loss resulted 20 % wt for neat pectin and 10%, 8%, 5% and 4% wt for 3%, 7.5%, 10% and 20% wt by weight of fiber loading respectively. The temperature range between 150 °C and 300 °C involves the thermal cracking of some bonds or functional groups, structural depolymerization and chains breaking along the polysaccharide [18]. Meantime, the same thermal range concerns the thermal decomposition of hemicellulose and pectin fractions present in the hemp fibers [19].

The hemp loading led to the shift of the main thermal event towards higher temperature (from 200 °C to 228 °C for pure pectin and pectin/HF 20% at 50%). The increase in thermal stability for pectin/hemp fibers biocomposites could be attributed to more factors. Firstly, the presence of lignin in hemp fibers, the most thermally stable fraction, contributed to increase the thermal stability of biocomposites [20]. Then, the interaction fiber-matrix due to hydrogen linkages might be responsible of the thermal decomposition delay. In fact, since the mechanochemical treatment removes external non-cellulosic materials, the roughness of treated hemp fibres surface tends to increase improving the interconnections between the hemp fibres and the polymeric matrix [21]. Besides, it is necessary to take into account the overlapping of heat and mass transfer phenomena that occur during the degradation [22]. As the fiber loading increases, the decomposition of low molecular compounds at low temperatures, partially formed by mechanochemical treatment, generates a noticeable amount of char which constitute a physical hindrance between the heat source and the polymer [23]. This barrier could serve as a physical barrier shielding the diffusion of combustible products (i.e. volatile gases) from oxygen and heat, contributing to increase the thermal stability of the composite. As a consequence, a reduction of decomposition rate and the slowing down of further thermal breakdown occurred since the reduction of heat flow and energy exchange [24]. Based on the above statements, it could be claimed that the presence

of hemp fibers could impede the thermal oxidative degradation of biocomposites.

The mechanical characterization was carried out on all samples and pure pectin, taken as reference, to investigate the effect of hemp fiber loading on mechanical properties of biocomposites. In fact, fiber loading, adhesion and interface properties were found to change and dominate the failure mechanism of the composites [25,26]. Fig. 2a shows the stress-strain curves that allowed to determine the elastic modulus, E (MPa) (Fig. 2b), the stress at the breakpoint, σ_{break} (MPa) (Fig. 2c), and the elongation at break, ϵ_{break} (mm/mm %) (Fig. 2d). Results obtained from the mechanical characterization displayed an increase in either the elastic modulus (up to 800% for a reinforcement loading of 20%wt) or the stress at break point (up to 300% for a reinforcement loading of 20%wt), proving the effect of hemp fibers as reinforcement agent. The effect of mechanochemical treatment could determine an increase in available surface area of hemp fibers and, so, an improvement of mechanical interlocking. It follows an enhanced high load transfer which could justify the increase in mechanical properties. Finally, a decrease in elongation at break point for the composites occurred resulting in a higher brittleness compared to the neat film.

3.2. Mechanical characterization

Mathematical modeling was applied to describe and understand the effect of fiber loading on the considered mechanical properties. The effect of fiber loading on elastic modulus of pectin composites was analyzed through the Nielsen model which is considered the most versatile model for short fibers reinforced composites. Such model (Eq. (1)) takes into account the filler packing, represented by parameter ψ [27]:

$$E_c = E_m * \left(\frac{1 + A\eta\phi_f}{1 - \eta\psi\phi_f} \right) \quad (1)$$

where ϕ_f is the fiber volume fraction and η is a function of the

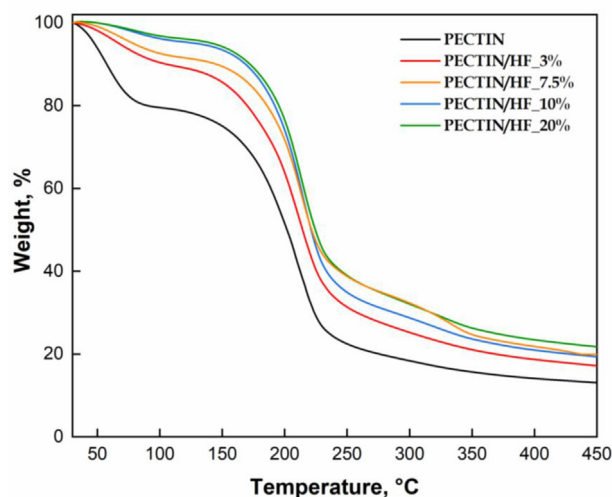


Fig. 1 – Thermogravimetric curves of neat pectin and biocomposites.

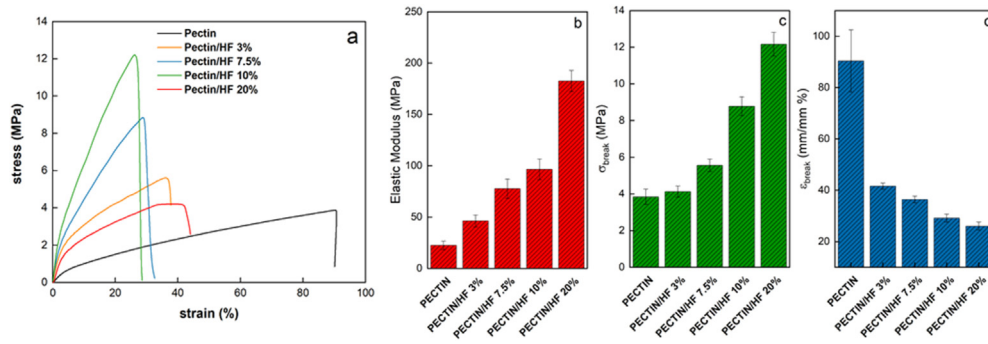


Fig. 2 – a) Stress–strain curves of neat pectin and biocomposites; b), c) and d) Mechanical parameters of neat pectin and biocomposites.

tensile moduli of fibres and matrix ($E_f = 32$ GPa and $E_m = 22.56$ MPa, respectively) (Eq. (2)):

$$\eta = \frac{\left(\frac{E_f}{E_m} - 1\right)}{\left(\frac{E_f}{E_m} + A\right)} \quad (2)$$

The parameter A is related to the Einstein coefficient (k), which is a function of the aspect ratio and orientation of the filler [27]:

$$A = k - 1$$

The generalized Einstein coefficient can be defined, as reported by Nilesen et al. [28], in Eq. (3):

$$k = \frac{d\left(E_c/E_m - 1\right)}{d\varphi_f} \quad (3)$$

Eq. (3) allowed to obtain $k = 98.84$ and $A = 97.84$. The parameter ψ is introduced to consider the fiber–fiber interaction while the quantity $\psi^* \varphi_f$ represents a reduced volume fraction of the reinforcement. An empirical form of ψ is proposed (Eq. (4)):

$$\psi = \frac{1}{\varphi_f} \left[1 - \exp\left(\frac{-\varphi_f}{1 - \frac{\varphi_f}{\varphi_m}}\right) \right] \quad (4)$$

The parameter φ_m represents the maximum packing fraction and it is based on filler shape and the maximum packing [27]. In a random short fiber system, it is function of the aspect ratio [29]. For three dimensional random fiber system, φ_m can be considered equal to 0.52 [30,31]. Substituting Eqs. (2) and (4) in Eq. (1), the elastic modulus of composites can be evaluated through Eq. (5):

$$E_c = E_m^* \left\{ \frac{1 + A\varphi_f \left(\frac{E_f}{E_m} - 1\right)}{\left(\frac{E_f}{E_m} + A\right)} \right\} \left[1 - \frac{\left(\frac{E_f}{E_m} - 1\right)}{\left(\frac{E_f}{E_m} + A\right)} * \left[1 - \exp\left(\frac{-\varphi_f}{1 - \frac{\varphi_f}{\varphi_m}}\right) \right] \right] \quad (5)$$

Fig. 3 reports the fitting process of experimental elastic modulus data through the application of Eq. (5).

Nielsen's model, widely applied for short fiber reinforced composites, well fitted the experimental data ($R^2 = 0.991$). It confirmed that, as the hemp fibers content increases, the elastic modulus increases up to a maximum fiber volume threshold beyond which composite properties deteriorate. This limit for the designed composite is roughly 25% w/w. The improvement of elastic modulus as the fiber content increases could be due to the presence of side-chain hydroxyl and polar groups of the hemp fiber responsible of a good adhesion with the hydrophilic matrix. It is worth to note that being the hemp fiber treated 30 min highly crystalline [14], the fibrils tend to rearrange themselves along with the tensile deformation leading to a better load sharing and transfer between fiber–fiber and fiber–matrix. The improved load transfer and the better adhesion, corresponding to continuity of stresses and displacements at the interface, led to an increases in the tensile strength of biocomposites [32,33]. The effect of fiber loading on tensile strength of pectin composites was described using the Pukànszky model [34] (Eq. (6)):

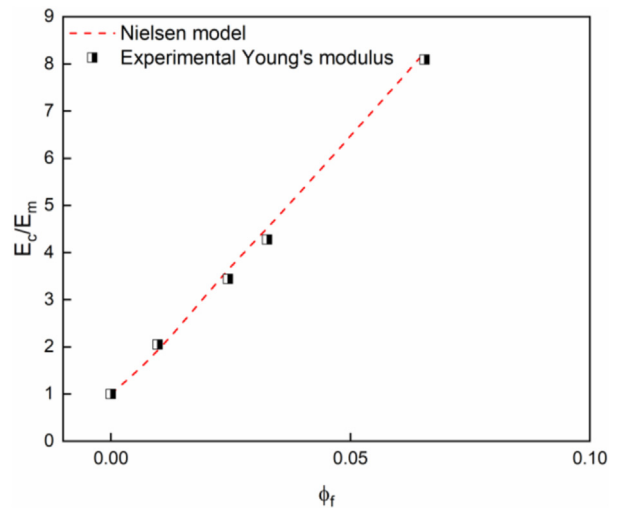


Fig. 3 – Fitting of experimental Young's modulus data through Eq. (5).

$$\frac{\sigma_c}{\sigma_m} = \frac{1 - \phi_f}{1 + A * \phi_f} * \exp(B * \phi_f) \tag{6}$$

where σ_c and σ_m are the tensile strength of composites and polymeric matrix, ϕ_f is the fiber volume fraction while B represents an interaction parameter related to the macroscopic characteristics of filler-matrix interface [32,34]. A is a parameter which depends on filler shape, size distribution and packing [34]. It is usually known for packed filler with spherical shape but, in our case, the unknown fiber distribution and orientation imposed to consider it in the fitting process. The first term on the right side of Eq. (1) accounts for the decrease of the effective load-bearing cross-section owing to the introduction of the filler into the polymer matrix [35] while the exponential one accounts for the interfacial properties of the given system. A and B parameters can be evaluated from the fitting process (Fig. 4). Fig. 4 shows the fitting of experimental data of the tensile strength values of fiber composites, normalized respect to tensile strength of neat pectin, with the Pukànszky model that well fits the experimental data.

Since the parameter B in the model represents the strength of interaction between the reinforcement and the polymeric matrix, the higher is B value the better is the interaction [32]. Low values of B ($B < 3$) are indication of weak interactions between the interfaces of biocomposites' components [36]. As expected, the force needed to break the composites was higher than for pure pectin due to the very high strength of the filler, and in good agreement with previously reported works [37]. The effect of fiber loading on elongation at break point of pectin composites was described considering the Smith model [38]. It was proposed in a modified form as expressed by Eq. (7):

$$\epsilon_c = \epsilon_m * (1 - \alpha * \phi_f^\beta) \tag{7}$$

The α and β parameters concern the geometrical properties of fiber arrays. Both were evaluated through the non linear fitting process. Fig. 5 reports the experimental data of the

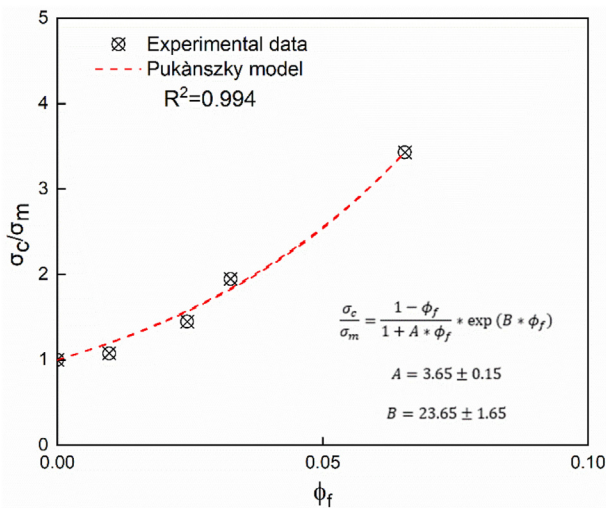


Fig. 4 – Fitting process of normalized experimental tensile strength of composites as function of fiber volume fraction through the application of Pukànszky model (Eq. (6)).

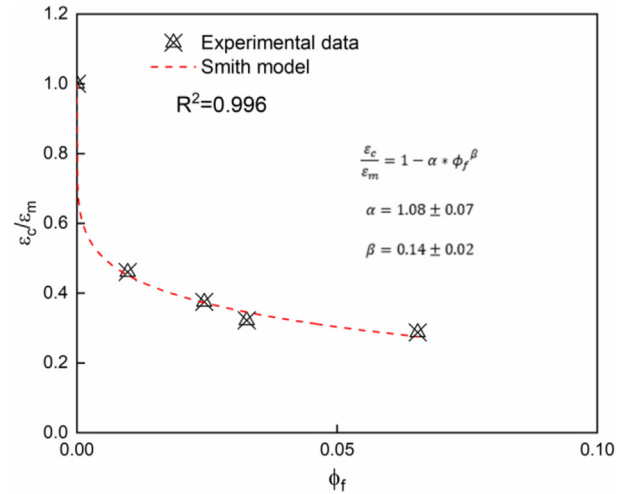


Fig. 5 – Fitting process of normalized experimental elongation at break point of composites as function of fiber volume fraction through the application of Smith model (Eq. (7)).

normalized elongation at break point of fiber composites, respect to the elongation at break point of neat pectin, with the modified Smith model.

As expected, elongation at break point for the composites is lower than the pure pectin. However, due to the formation of a compact structure consequent to high intermolecular hydrogen bond interconnections, the reinforced composites resulted more brittle than the neat film [39]. Moreover, no noticeable differences between the reinforced composites can be observed. Finally, the evaluation of strain energy density (SED) was carried out by calculating the area under the stress–strain curve (Fig. 6). It provides a measure of the energy adsorbed by the material during the tensile test and, so, an indication of the resistance to the break [16]. For low filler loading (3%) it can be observed a decrease in SED (Fig. 6). As the fiber loading increases, the rich fiber population induced an

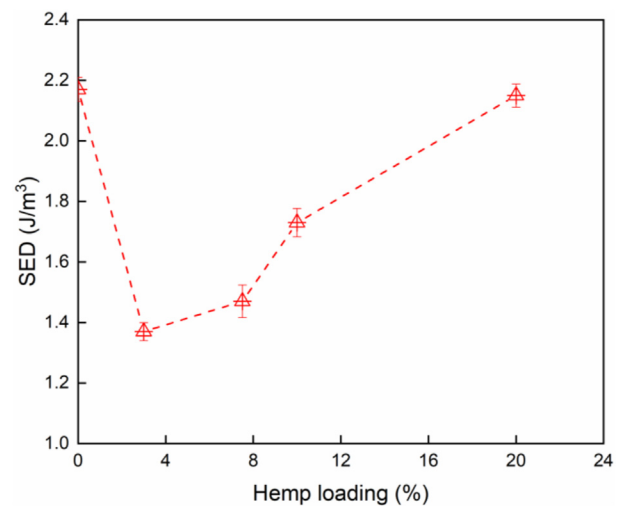


Fig. 6 – Strain energy density (J/m³) as a function of hemp fiber loading (%).

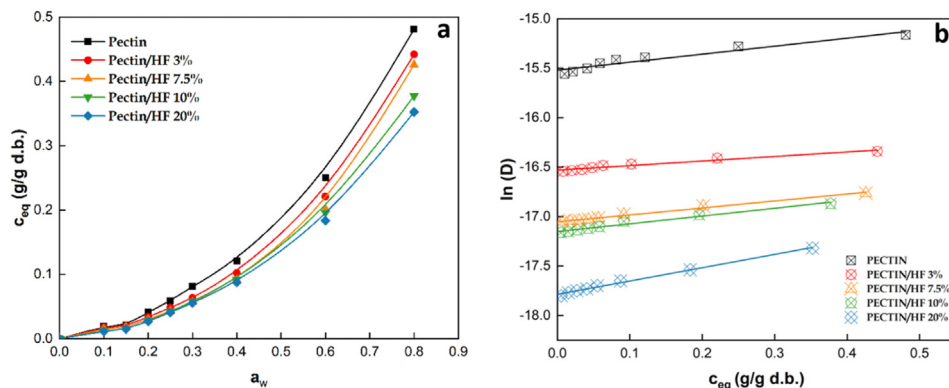


Fig. 7 – (a) Equilibrium water vapor sorption, C_{eq} (g/g d.b.), as function of water activity, a_w ; (b) $\ln(D)$ as function of equilibrium water vapor sorption, C_{eq} (g/g d.b.), for neat pectin and biocomposites.

improved load transfer capacity among the fiber–fiber and the fiber-matrix [40]. Moreover, it is worthwhile to claim that no drop in mechanical properties at higher loading was verified.

The high energy ball milling process, used for filler dispersion, was able to allow a good distribution of hemp fibers in pectin matrix with resulting improved mechanical performances. We can hypothesize a good load transfer from pectin to hemp fibers and the increase in Young's modulus and stress at break point could be an indication that agglomerates are avoided in the used processing conditions. As for the mechanical characterization, the change in the barrier properties of pectin composites was investigated and correlated to hemp fiber loading. Fig. 7a reports the sorption isotherms of the neat pectin and pectin/HF composites, as C_{eq} (g on dry basis (d.b.)) versus water activity (a_w).

The adsorption isotherms demonstrate an increase in equilibrium moisture content with increasing water activity, at constant temperature. This behaviour is manifested in the form of Type II isotherm, according to Brunauer's classification [41]. The sorption parameters (S) were obtained from the equilibrium concentration (C_{eq}) of the permeant vapor as a function of the partial pressure (Eq. (8)).

$$S = \frac{dc_{eq}}{dp} \quad (8)$$

They were evaluated by the linear part of sorption isotherms, considering that $a_w = P/P_0$. Table 1 reports the

Table 1 – Sorption, diffusion and permeability coefficients of pectin and bio-composites.

Sample	S g/g d.b. atm ⁻¹	D_0 10 ⁷ cm ² s ⁻¹	P 10 ⁷ g/g d.b. atm ⁻¹ cm ² *s ⁻¹
Pectin	7.65	1.25	9.56
Pectin/HF 3%	6.10	0.62	3.78
Pectin/HF 7.5%	6.01	0.39	2.36
Pectin/HF 10%	5.75	0.36	2.04
Pectin/HF 20%	5.65	0.19	1.06

sorption values for the neat pectin and pectin/hemp fibers biocomposites.

In agreement with the TGA results (evaluation of loss of water), it is evident that the sorption of water decrease in the biocomposites with filler loading. This behavior was related to the less hydrophilic character of the fibers in comparison to pectin's highly hydrophilic property. The higher the fiber content, the less the water absorbed. It was demonstrated that the mechanochemical treatment of hemp fiber, for very short time, led to a highly crystalline regions which showed a good resistance to small waters' molecules penetration [42]. The presence of OH sites from hemp fibers contributed to the chemical interactions with polar groups of pectin matrix leading to an improvement of the interfacial adhesion properties. The Guggenheim, Anderson, de Boer equation (GAB) was used to correlate the sorption data in the whole investigated range of activities. The model allowed to describe the shape of type II isotherm [43]. A modified GAB equation, is expressed by Eq. (9) which accounts for the heterogeneity of the adsorption surface expressed by parameter n [44]

$$w = \frac{w_m * C * K * a_w^n}{(1 - K * a_w^n) (1 - K * a_w^n + c * K * a_w^n)} \quad (9)$$

where w represents the moisture content evaluated respect to the dry basis weight, a_w is the water activity while w_m takes into consideration the monolayer moisture content, K is a dimensionless parameter that refers to the heat of the sorption of the multilayer region, while c is related to the heat of the sorption of the monolayer region Table 2 reports the evaluated GAB sorption parameter, using Eq. (9) to fit the experimental data, with the correlation coefficient (R^2) c and K

Table 2 – Sorption parameters evaluated from the modified GAB model.

Sample	w_m (g/g d.b.)	C	K	n	R^2
Pectin	0.26	3.12	0.79	1.65	0.996
Pectin/HF 3%	0.22	2.51	0.78	1.71	0.998
Pectin/HF 7.5%	0.21	2.40	0.76	1.84	0.996
Pectin/HF 10%	0.19	2.38	0.76	2.09	0.995
Pectin/HF 20%	0.17	2.29	0.72	2.12	0.996

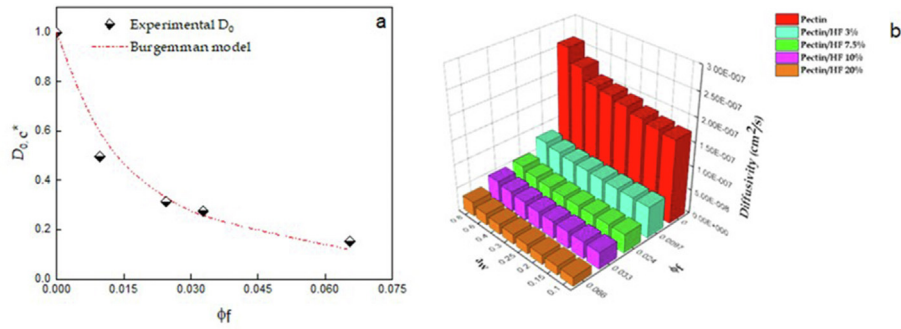


Fig. 8 – (a) Fitting process of D_0 experimental data and (b) Dependence of Diffusivity on water activity and fiber volume fraction.

values are affected by the geometrical shape of sorption isotherms.

The c value is related to the “knee” of the curve while K value determines the curvature of the sorption isotherm at higher values of a_w [45]. The w_m parameter, which represents the maximum monolayer water capacity, decreased due to the reduction of available accessible primary sorption sites due to the OH interactions between the matrix and the fibers. In addition, since w_m is directly proportional to the internal specific area, it is possible to hypothesize that the presence of hemp fibers reduced the internal specific area of the composites system [45]. The diffusion coefficient can be evaluated from sorption kinetics, using Fick’s second law solution. From the mass transfer balance, without considering the convection contribution and the diffusion along the edges, the Fick’s second law can be expressed from Eq. (10):

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \tag{10}$$

where x is the spatial coordinate considering the process isotropic one-dimensional. To be solved, the equation requires two spacial boundary conditions and one boundary condition on time. Considering the permeation through a thin membrane, the equation admits the following solution (Eq. (11)) [46]:

$$\frac{c - c_i}{c_{eq} - c_i} = 1 - \frac{4}{\pi} \sum_{j=0}^{\infty} \frac{1}{(2j + 1)^2} \frac{\sin(2j + 1)\pi x}{d} \exp \left[-\frac{(2j + 1)^2 \pi^2 Dt}{d^2} \right] \tag{11}$$

where C_i is the initial concentration inside the sample, C_{eq} is the maximum saturation concentration, d is the characteristic length of the sample, and D (cm^2/s) the diffusion coefficient. In order to evaluate the penetrant concentration at the time t , the above Eq. (10) can be integrated over length x (Eq. (12)):

$$\frac{m - m_i}{m_{eq} - m_i} = 1 - \frac{8}{\pi^2} \sum_{j=1}^{\infty} \frac{1}{(2j + 1)^2} \exp \left[-\frac{(2j + 1)^2 \pi^2 Dt}{d^2} \right] \tag{12}$$

with m_i = initial mass of moisture and m_{eq} = mass of moisture when saturation is reached. Fig. 7b reports the $\ln(D)$ as a

function of the equilibrium moisture content (C_{eq} , g/g on d.b.). It is clearly evident that the diffusion coefficient of bio-composites decrease with filler loading. This could be, firstly, explained by taking into account the interactions fiber-matrix, mainly hydrogen bondings, with hydrophilic groups of pectin matrix. Moreover, from transport phenomena point of view, as the fiber loading increases the mass transfer resistance offered by them increases due to the barrier effect which, likely, led to a reduction of mean cross sectional area available for water diffusion. Table 1 reports the D_0 , the thermodynamic diffusion coefficients extrapolated at $C_{eq} = 0$, for all the samples. From Eq. (13), it is possible to evaluate the water permeability coefficients (reported in Table 2)

$$P = S * D_0 \tag{13}$$

As expected, from S and D_0 data, permeability of bio-composites decreases with filler loading, and such decrement is mainly due to the diffusion. The correlation between D_0 and the fibers volume fraction was investigated through the application of a mathematical model developed by Bruggemann that was used to evaluate the effective thermal conductivity of two-phase systems [47]. Exploiting the analogy between heat and mass transfer, the same model was applied the analysed systems. In order to consider the non-spherical shape of dispersed phase, Burgemman equation was corrected by Fricke [48] through the introduction of an empirical parameter, X , which concerns the aspect ratio ($L/d = \text{length/diameter}$) of the fibers. The modified model is expressed from Eq. (14):

$$\left(D_{0,c}^* \right)^{\frac{1}{X+1}} * (1 - \varphi_f) = \left(D_{0,c}^* - D_{0,f}^* \right) * \left(1 - D_{0,f}^* \right)^{-1} \tag{14}$$

where $D_{0,c}^*$ and $D_{0,f}^*$ are the D_0 diffusivities of composites and hemp fibers, respectively, normalized respect to the D_0 coefficient of neat pectin, while φ_f is the fiber volume fraction. The hemp fiber D_0 coefficient belongs from the already reported study of transport properties of water vapor on raw and mechanochemically treated HF where the value used to performe the mathematical modeling of diffusivity-fiber volume fraction relationship was found to be $7.05 * 10^{-9} \text{ cm}^2/\text{s}$. Fig. 8a

shows the fitting process ($R^2 = 0.989$) of thermodynamic diffusion coefficients (D_0) as function of the fiber volume fraction, and Fig. 8b reports the dependence of the diffusion coefficient (D) on either water activity or fiber volume fraction. The error percent between the experimental data and the predicted values allows to observe that the Burgeman model, accounting for no-sphericity of filler, appeared to well fit the experimental data ($R^2 = 0.989$). The parameter $X+1$ resulted to be equal to 0.898 ± 0.012 .

4. Conclusions

Biocomposites obtained from natural pectin from apple and mechanochemical treated hemp fibers, as green filler, have been obtained and the dependence of fiber loading (3%; 7.5%; 10%; 20% w/w by weight) on their thermal, barrier and mechanical properties was investigated. Thermogravimetric analyses (TGA) demonstrated the improvement in thermal stability of reinforced pectin films compared to pure pectin one (about 50 °C at 95% and 30 °C at 50% with 20% w/w of HF) which could be attributed to a good interaction between fibers' OH sites and polar groups of pectin matrix. As a results, the improved adhesion filler-matrix induced a shift of the main thermal decomposition step towards higher temperatures. The effect of fiber loading on the mechanical properties demonstrated a significant improvement of elastic modulus (up to 180 MPa for 20% w/w) and tensile strength (up to 13 MPa for 20% w/w), and data fitted using Nielsen and Pukánszky models, taking into account filler's geometrical factors. The analysis of barrier properties to water vapour (sorption, diffusion and permeability) showed a decrease in sorption (about 26% at 20% w/w) and diffusion (about 85% at 20% w/w), compared to unfilled pectin film. The inclusion of hemp fiber in the pectin matrix results in a decrease of its hydrophilic character and capacity of water uptake. The OH bonding interconnections involving filler and matrix, the less availability of free sites for water adsorption and the hindrance due to the fiber array distribution, allowed to justify the important improvement of barrier properties as fiber loading increased. Being very difficult both mechanically reinforce and improve the barrier properties respect to moisture in composites from green and renewable sources, without using expensive surface barriers, the inclusion of treated natural hemp fibers has been demonstrated to be an efficient and cheap solution.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

The project Prin 2017 "MultiFunctional polymer composites based on grown materials (MIFLOWER)" (grant number:

2017B7MMJ5_001) from the Italian Ministry of University and Research is kindly acknowledged.

REFERENCES

- [1] Sanjay MR, Siengchin S, Parameswaranpillai J, Jawaid M, Pruncu CI, Khan A. A comprehensive review of techniques for natural fibers as reinforcement in composites: preparation, processing and characterization. *Carbohydr Polym* 2019;207:108–21. <https://doi.org/10.1016/j.carbpol.2018.11.083>.
- [2] Zhang Z, Cai S, Li Y, Wang Z, Long Y, Yu T, et al. High performances of plant fiber reinforced composites—a new insight from hierarchical microstructures. *Compos Sci Technol* 2020;194:108151. <https://doi.org/10.1016/j.compscitech.2020.108151>.
- [3] Neves ACC, Rohen LA, Mantovani DP, Carvalho JPRG, Vieira CMF, Lopes FPD, et al. Comparative mechanical properties between biocomposites of Epoxy and polyester matrices reinforced by hemp fiber. *J Mater Res Technol* 2020;9:1296–304. <https://doi.org/10.1016/j.jmrt.2019.11.056>.
- [4] Dang V, Nguyen KL. Characterisation of the heterogeneous alkaline pulping kinetics of hemp woody core. *Bioresour Technol* 2006;97:1353–9. <https://doi.org/10.1016/j.biortech.2005.07.008>.
- [5] Wang HM, Postle R, Kessler RW, Kessler W. Removing pectin and lignin during chemical processing of hemp for textile applications. *Textil Res J* 2003;73:664–9. <https://doi.org/10.1177/004051750307300802>.
- [6] Viscusi G, Barra G, Verdolotti L, Galzerano B, Viscardi M, Gorrasi G. Natural fiber reinforced inorganic foam composites from short hemp bast fibers obtained by mechanical decortation of unretted stems from the wastes of hemp cultivations. *Mater Today Proc* 2020;34:176–9. <https://doi.org/10.1016/j.matpr.2020.02.672>.
- [7] Bessadok A, Langevin D, Gouanvé F, Chappey C, Roudesli S, Marais S. Study of water sorption on modified Agave fibres. *Carbohydr Polym* 2009;76:74–85. <https://doi.org/10.1016/j.carbpol.2008.09.033>.
- [8] Pejić BM, Kramar AD, Obradović BM, Kuraica MM, Žekić AA, Kostić MM. Effect of plasma treatment on chemical composition, structure and sorption properties of lignocellulosic hemp fibers (*Cannabis sativa* L.). *Carbohydr Polym* 2020;236:116000. <https://doi.org/10.1016/j.carbpol.2020.116000>.
- [9] Dou J, Paltakari J, Johansson LS, Vuorinen T. Novel insight into the separation and composite utilization of sclerenchyma fiber bundles of willow bark. *ACS Sustainable Chem Eng* 2019;7:2964–70. <https://doi.org/10.1021/acssuschemeng.8b04001>.
- [10] Agate S, Tyagi P, Naithani V, Lucia L, Pal L. Innovating generation of nanocellulose from industrial hemp by dual asymmetric centrifugation. *ACS Sustainable Chem Eng* 2020;8:1850–8. <https://doi.org/10.1021/acssuschemeng.9b05992>.
- [11] Panaitescu DM, Fierascu RC, Gabor AR, Nicolae CA. Effect of hemp fiber length on the mechanical and thermal properties of polypropylene/SEBS/hemp fiber composites. *J Mater Res Technol* 2020;9:10768–81. <https://doi.org/10.1016/j.jmrt.2020.07.084>.
- [12] Oudiani A El, Chaabouni Y, Msahli S, Sakli F. Crystal transition from cellulose I to cellulose II in NaOH treated Agave americana L. fibre. *Carbohydr Polym* 2011;86:1221–9. <https://doi.org/10.1016/j.carbpol.2011.06.037>.

- [13] Haghghatnia T, Abbasian A, Morshedian J. Hemp fiber reinforced thermoplastic polyurethane composite: an investigation in mechanical properties. *Ind Crop Prod* 2017;108:853–63. <https://doi.org/10.1016/j.indcrop.2017.07.020>.
- [14] Viscusi G, Barra G, Gorrasi G. Modification of hemp fibers through alkaline attack assisted by mechanical milling: effect of processing time on the morphology of the system. *Cellulose* 2020;27:8653–65. <https://doi.org/10.1007/s10570-020-03406-0>.
- [15] Liu J, Guan Z, Li Z. Application of cryogenic and mechanical treatment in degumming of hemp stems. *Biosyst Eng* 2018;174:144–52. <https://doi.org/10.1016/j.biosystemseng.2018.07.007>.
- [16] Rojo E, Alonso MV, Oliet M, Del Saz-Orozco B, Rodriguez F. Effect of fiber loading on the properties of treated cellulose fiber-reinforced phenolic composites. *Compos B Eng* 2015;68:185–92. <https://doi.org/10.1016/j.compositesb.2014.08.047>.
- [17] Gorrasi G. Dispersion of halloysite loaded with natural antimicrobials into pectins: characterization and controlled release analysis. *Carbohydr Polym* 2015;127:47–53. <https://doi.org/10.1016/j.carbpol.2015.03.050>.
- [18] Aburto J, Moran M, Galano A, Torres-García E. Non-isothermal pyrolysis of pectin: a thermochemical and kinetic approach. *J Anal Appl Pyrolysis* 2015;112:94–104. <https://doi.org/10.1016/j.jaap.2015.02.012>.
- [19] Kabir MM, Wang H, Lau KT, Cardona F. Effects of chemical treatments on hemp fibre structure. *Appl Surf Sci* 2013;276:13–23. <https://doi.org/10.1016/j.apsusc.2013.02.086>.
- [20] Fisher T, Hajaligol M, Waymack B, Kellogg D. Pyrolysis behavior and kinetics of biomass derived materials. *J Anal Appl Pyrolysis* 2002;62:331–49. [https://doi.org/10.1016/S0165-2370\(01\)00129-2](https://doi.org/10.1016/S0165-2370(01)00129-2).
- [21] Viscusi G, Pantani R, Gorrasi G. Transport properties of water vapor through hemp fibers modified with a sustainable process: effect of surface morphology on the thermodynamic and kinetic phenomena. *Appl Surf Sci* 2021;541:148433. <https://doi.org/10.1016/j.apsusc.2020.148433>.
- [22] Sánchez-Jiménez PE, Pérez-Maqueda LA, Perejón A, Criado JM. Combined kinetic analysis of thermal degradation of polymeric materials under any thermal pathway. *Polym Degrad Stabil* 2009;94:2079–85. <https://doi.org/10.1016/j.polymdegradstab.2009.07.006>.
- [23] Hurley MJ, Gottuk D, Hall JR, Harada K, Kuligowski E, Puchovsky M, et al. *SFPE handbook of fire protection engineering*. 5th ed. New York: Springer; 2016. <https://doi.org/10.1007/978-1-4939-2565-0>.
- [24] Weil ED, Hansen RH, Patel N. Prospective approaches to more efficient flame-retardant systems. 1990. p. 97–108. <https://doi.org/10.1021/bk-1990-0425.ch008>.
- [25] Wan YZ, Luo H, He F, Liang H, Huang Y, Li XL. Mechanical, moisture absorption, and biodegradation behaviours of bacterial cellulose fibre-reinforced starch biocomposites. *Compos Sci Technol* 2009;69:1212–7. <https://doi.org/10.1016/j.compscitech.2009.02.024>.
- [26] Munirah Abdullah N, Ahmad I. Effect of chemical treatment on mechanical and water-sorption properties coconut fiber-saturated polyester from recycled PET. *Int Sch Res Netw ISRN Mater Sci* 2012;2012. <https://doi.org/10.5402/2012/134683>.
- [27] Loos M. Fundamentals of polymer matrix composites containing CNTs. In: *Carbon nanotub. Reinf. Compos. CNR polym. Sci. Technol.* Elsevier Inc.; 2015. p. 125–70. <https://doi.org/10.1016/B978-1-4557-3195-4.00005-9>.
- [28] Nielsen LE. Generalized equation for the elastic moduli of composite materials. *J Appl Phys* 1970;41:4626–7. <https://doi.org/10.1063/1.1658506>.
- [29] Milewski JV, Katz HS. *Handbook of reinforcements for plastics*. Van Nostrand Reinhold Co; 1987.
- [30] Nielsen LE. The thermal and electrical conductivity of two-phase systems. *Ind Eng Chem Fundam* 1974;13:17–20. <https://doi.org/10.1021/i160049a004>.
- [31] Keith JM, King JA, Miskioglu I, Roache SC. Tensile modulus modeling of carbon-filled liquid crystal polymer composites. *Polym Compos* 2009;30:1166–74. <https://doi.org/10.1002/pc.20673>.
- [32] Demir H, Atikler U, Balköse D, Tihminlioğlu F. The effect of fiber surface treatments on the tensile and water sorption properties of polypropylene-luffa fiber composites. *Compos Part A Appl Sci Manuf* 2006;37:447–56. <https://doi.org/10.1016/j.compositesa.2005.05.036>.
- [33] Hull D, Clyne TW. *An introduction to composite materials*. Cambridge University Press; 1996. <https://doi.org/10.1017/cbo9781139170130>.
- [34] Pukánszky B, Tüdös F, Jančar J, Kolařík J. The possible mechanisms of polymer-filler interaction in polypropylene-CaCO₃ composites. *J Mater Sci Lett* 1989;8:1040–2. <https://doi.org/10.1007/BF01730480>.
- [35] Kiran MD, Govindaraju HK, Jayaraju T, Kumar N. Review-effect of fillers on mechanical properties of polymer matrix composites. In: *Mater. Today proc.*, vol. 5. Elsevier Ltd; 2018. p. 22421–4. <https://doi.org/10.1016/j.matpr.2018.06.611>.
- [36] Sideridis E, Kytopoulos VN, Papadopoulos GA, Bourkas GD. The effect of low-filler volume fraction on the elastic modulus and thermal expansion coefficient of particulate composites simulated by a multiphase model. *J Appl Polym Sci* 2009;111:203–16. <https://doi.org/10.1002/app.28886>.
- [37] Dias AB, Müller CMO, Larotonda FDS, Laurindo JB. Mechanical and barrier properties of composite films based on rice flour and cellulose fibers. *LWT - Food Sci Technol (Lebensmittel-Wissenschaft - Technol)* 2011;44:535–42. <https://doi.org/10.1016/j.lwt.2010.07.006>.
- [38] Smith TL. Volume changes and dewetting in glass bead-polyvinyl chloride elastomeric composites under large deformations. *Trans Soc Rheol* 1959;3:113–36. <https://doi.org/10.1122/1.548847>.
- [39] Bodirlau R, Teaca CA, Spiridon I. Influence of natural fillers on the properties of starch-based biocomposite films. *Compos B Eng* 2013;44:575–83. <https://doi.org/10.1016/j.compositesb.2012.02.039>.
- [40] Khan JA, Khan MA, Islam R. Mechanical, thermal and degradation properties of jute fabric - reinforced polypropylene composites: effect of potassium permanganate as oxidizing agent. *Polym Compos* 2013;34:671–80. <https://doi.org/10.1002/pc.22470>.
- [41] Brunauer S, Deming LS, Deming WE, Teller E. On a theory of the van der Waals adsorption of gases. *J Am Chem Soc* 1940;62:1723–32. <https://doi.org/10.1021/ja01864a025>.
- [42] Al-Muhtaseb AH, McMinn WAM, Magee TRA. Water sorption isotherms of starch powders: Part 1: mathematical description of experimental data. *J Food Eng* 2004;61:297–307. [https://doi.org/10.1016/S0260-8774\(03\)00133-X](https://doi.org/10.1016/S0260-8774(03)00133-X).
- [43] Timmermann EO. Multilayer sorption parameters: BET or GAB values? *Colloids Surfaces A Physicochem Eng Asp* 2003;220:235–60. [https://doi.org/10.1016/S0927-7757\(03\)00059-1](https://doi.org/10.1016/S0927-7757(03)00059-1).
- [44] Zou L, Gong L, Xu P, Feng G, Liu H. Modified GAB model for correlating multilayer adsorption equilibrium data. *Separ Purif Technol* 2016;161:38–43. <https://doi.org/10.1016/j.seppur.2016.01.026>.
- [45] Bratasz Kozłowska A, Kozłowski R. Analysis of water adsorption by wood using the Guggenheim-Anderson-de Boer equation. *Eur J Wood Wood Prod* 2012;70:445–51. <https://doi.org/10.1007/s00107-011-0571-x>.

- [46] Shen C-H, Springer GS. Moisture absorption and desorption of composite materials. *J Compos Mater* 1976;10:2–20. <https://doi.org/10.1177/002199837601000101>.
- [47] Yamada E, Ota T. Effective thermal conductivity of dispersed materials. *Wärme- Und Stoffübertragung* 1980;13:27–37. <https://doi.org/10.1007/BF00997630>.
- [48] Fricke H. A mathematical treatment of the electric conductivity and capacity of disperse systems I. The electric conductivity of a suspension of homogeneous spheroids. *Phys Rev* 1924;24:575–87. <https://doi.org/10.1103/PhysRev.24.575>.