

Modelling of volumetric composition and mechanical properties of unidirectional hemp/epoxy composites - Effect of enzymatic fibre treatment

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Abstract. The objective of the present study is to assess the effect of enzymatic fibre treatments on the fibre performance in unidirectional hemp/epoxy composites by modelling the volumetric composition and mechanical properties of the composites. It is shown that the applied models can well predict the changes in volumetric composition and mechanical properties of the composites when differently treated hemp fibres are used. The decrease in the fibre correlated porosity factor with the enzymatic fibre treatments shows that the removal of pectin by pectinolytic enzymes results in a better fibre impregnation by the epoxy matrix, and the mechanical properties of the composites are thereby increased. The effective fibre stiffness and strength established from the modelling show that the enzymatic removal of pectin also leads to increased mechanical properties of the fibres. Among the investigated samples, the composites with hydrothermally pre-treated and enzymatically treated fibres have the lowest porosity factor of 0.08 and the highest mechanical properties. In these composites, the effective fibre stiffness and strength are determined to be 83 GPa and 667 MPa, respectively, when the porosity efficiency exponent is set equal to 2. Altogether, it is demonstrated that the applied models provide a concept to be used for the evaluation of performance of treated fibres in composites.

1. Introduction

As a result of increasing environmental awareness, research interest has been shifting to use natural fibres as substitute to man-made fibres in fibre reinforced composites due to their unique advantages, such as environmental sustainability, low cost, low density, together with their high stiffness and strength to weight ratio [1,2]. However, their potential use as reinforcement could be considerably reduced by some of their disadvantages including moderate strength of fibres, less controlled processing methods, and seasonal variation in quality [3–5].

In principle, the aim of fibre processing is to obtain more separated and cellulose rich fibres by removing non-cellulosic components, in order to optimize the strength and form of the fibres before being used as reinforcement in composites. Traditional cellulose fibre processing methods for hemp and flax fibres, which have mainly been targeted for yarn production, include field retting and water retting. These retting methods remove non-cellulosic components via spontaneously flourishing microbial activity, and they have been reported to have negative impacts on both fibre properties and the environment [5,6]. As an alternative method, treatment of fibres with pectinolytic enzymes could



be a more efficient and controlled method, in addition to overcoming the limitations of the traditional fibre processing methods [7–9].

Porosity is a parameter that is used to assess the quality of composites. Porosity in natural fibre composites is not only created due to insufficient impregnation of the fibres by the matrix, but also due to the air filled cavities inside the fibres, the so-called lumen. Porosity has a direct influence on the volumetric composition (i.e. the volume contents of fibres and matrix) and the mechanical properties of composites [9–11]. A study of the relations between fibre processing routes, and the volumetric composition and mechanical properties of composites is central to the goal of assessing the effect of various fibre treatments.

In the present study, enzymatic treatments with and without hydrothermal pre-treatment were carried out on hemp bast fibres. For comparison, traditional field retting of fibres was also carried out [5]. It is expected that porosity is highest in the composites with the untreated fibres due to the presence of the epidermis layer and parenchyma cells, which consist of a large amount of voids [9,12]. In contrast, it is expected that the enzymatic treatments will produce fibres where the epidermis layer and part of parenchyma cells are removed, in addition to splitting larger fibre bundles into smaller ones [7,9,13]. Those changes are expected to decrease the porosity in the composites, and the mechanical properties will thereby be increased.

The objective of the present study is to use previously developed models for composite volumetric composition and mechanical properties for a quantitative analysis of the effect of enzymatically based fibre processing methods. This approach is shown to provide valuable understanding of the effect of the fibre treatments on the properties of the composites.

2. Model

In the present study, experimental data is modelled by previously reported models [11,14]. Experimental data for composite volumetric composition, density and mechanical properties (i.e. stiffness and strength) were obtained for composites with a fibre weight content (W_f) below the transition value ($W_{f\text{trans}}$). For the modelling of composites with W_f above $W_{f\text{trans}}$ only model lines will be shown. A summary of the applied model parameters is shown in Table 1. The parameters, fibre density (ρ_f), matrix density (ρ_m), matrix correlated porosity factor (α_{pm}), maximum obtainable fibre volume content ($V_{f\text{max}}$), and porosity efficiency exponent for composite stiffness (n_E) and strength (n_σ) are assumed to be constant and independent of the applied fibre treatments. The parameters, transition fibre weight content ($W_{f\text{trans}}$) and fibre correlated porosity factor (α_{pf}) are assumed to be dependent on the fibre treatment.

Table 1. Summary of model parameters applied in the present study.

Parameter	Meaning	Value	Way of determining the value
ρ_f	fibre density	1.50 g/cm ³	assumed
ρ_m	matrix density	1.14 g/cm ³	measured
α_{pm}	matrix correlated porosity factor	0	assumed
$V_{f\text{max}}$	maximum obtainable fibre volume content	0.65	assumed
n_E	porosity efficiency exponent for composite stiffness	0 or 2	assumed
n_σ	porosity efficiency exponent for composite strength	0 or 2	assumed
$W_{f\text{trans}}$	transition fibre weight content	see Table 2	determined from Eq.1
α_{pf}	fibre correlated porosity factor	see Table 2	determined from Eq.2

2.1. Volumetric composition

In the selected model [11], the volumetric composition in composites is correlated to the fibre weight content (W_f) in two regions: region A, where W_f is below a transition value ($W_{f \text{ trans}}$), and region B, where W_f is above a transition value ($W_{f \text{ trans}}$), respectively. The transition value ($W_{f \text{ trans}}$) separating region A and B is calculated by Eq.1.

$$W_{f \text{ trans}} = \frac{V_{f \text{ max}} \rho_f (1 + \alpha_{pm})}{V_{f \text{ max}} (1 + \alpha_{pm}) - V_{f \text{ max}} \rho_m (1 + \alpha_{pf}) + \rho_m} \quad (1)$$

In this study, it is assumed that there is no matrix correlated porosity in the composites, and therefore α_{pm} is set to 0. The fibre correlated porosity factor (α_{pf}) is determined by using Eq.2, where the porosity (V_p) is assumed to be a linear function of the fibre volume content (V_f) [11].

$$V_p = \alpha_{pf} \times V_f \quad (2)$$

The volumetric composition in the composites in region A and region B are shown in Eqs.3 – 8. Region A ($W_f \leq W_{f \text{ trans}}$)

$$V_f = \frac{W_f \rho_m}{W_f \rho_m (1 + \alpha_{pf}) + (1 - W_f) \rho_f (1 + \alpha_{pm})} \quad (3)$$

$$V_m = \frac{(1 - W_f) \rho_f}{W_f \rho_m (1 + \alpha_{pf}) + (1 - W_f) \rho_f (1 + \alpha_{pm})} \quad (4)$$

$$V_p = 1 - V_f - V_m = \frac{W_f \rho_m \alpha_{pf} + (1 - W_f) \rho_f \alpha_{pm}}{W_f \rho_m (1 + \alpha_{pf}) + (1 - W_f) \rho_f (1 + \alpha_{pm})} \quad (5)$$

Region B ($W_f \geq W_{f \text{ trans}}$)

$$V_f = V_{f \text{ max}} \quad (6)$$

$$V_m = V_{f \text{ max}} \frac{(1 - W_f) \rho_f}{W_f \rho_m} \quad (7)$$

$$V_p = 1 - V_f - V_m = 1 - V_{f \text{ max}} \left(1 + \frac{(1 - W_f) \rho_f}{W_f \rho_m} \right) \quad (8)$$

2.2. Composite density

Equations for composite density, Eqs.10 – 11, can be derived from Eq. 9 by using the expression for volumetric composition in composites.

$$\rho_c = \frac{m_c}{V_c} = \frac{m_f / W_f}{m_f / (\rho_f V_f)} = \frac{\rho_f V_f}{W_f} \quad (9)$$

Region A ($W_f \leq W_{f \text{ trans}}$)

$$\rho_c = \frac{\rho_m \rho_f}{W_f \rho_m (1 + \alpha_{pf}) + (1 - W_f) \rho_f (1 + \alpha_{pm})} \quad (10)$$

Region B ($W_f \geq W_{f \text{ trans}}$)

$$\rho_c = \frac{V_{f \text{ max}}}{W_f} \rho_f \quad (11)$$

In the modelling of composite density, the fibre weight content (W_f) is set as the independent variable, and composite density (ρ_c) is set as the dependent variable. The values of the other parameters are given in Tables 1 and 2. The experimental data of ρ_c vs. W_f is compared with the model predictions (Eqs. 10 – 11).

2.3. Mechanical properties

A large number of modified rule of mixtures models for stiffness of composites have been proposed in the literature [14,15]. In one of these models, by including the effect of porosity [14], stiffness (E_c) and strength (σ_{cu}) of composites with a unidirectional fibre orientation and with continuous fibres can be expressed by Eq.12 and Eq.13, respectively.

$$E_c = (V_f E_f + V_m E_m)(1 - V_p)^{n_E} \quad (12)$$

$$\sigma_{cu} = (V_f \sigma_{fu} + V_m \sigma_m^*)(1 - V_p)^{n_\sigma} \quad (13)$$

where E is the stiffness, V is the volume content, the subscripts c , m , f and p are composite, matrix, fibres and porosity, respectively. σ_{cu} is the composite strength, σ_{fu} is the fibre strength, and σ_m^* is the stress in the matrix at the failure strain of the composite, and n_E and n_σ are the porosity efficiency exponents (PEE) for stiffness and strength, respectively. When $PEE = 0$, it is assumed that the porosity in the composites has no effect on the mechanical properties of the composites beyond lowering the load bearing volume. When $PEE > 0$, it is assumed that the porosity in the composites has an effect on the mechanical properties of composites by introducing stress concentrations [14]. Values of PEE equal to 0 and 2 are used in the present study to show these two cases.

By using the models for the composite volumetric composition, equations for the correlation between composite stiffness (E_c) and strength (σ_{cu}) and the fibre weight fraction (W_f) can be established.

Region A ($W_f \leq W_{ftrans}$)

$$E_c = \frac{(W_f \rho_m E_f + (1 - W_f) \rho_f E_m)(W_f \rho_m + (1 - W_f) \rho_f)^{n_E}}{(W_f \rho_m (1 + \alpha_{pf}) + (1 - W_f) \rho_f (1 + \alpha_{pm}))^{n_E + 1}} \quad (14)$$

$$\sigma_{cu} = \frac{(W_f \rho_m \sigma_{fu} + (1 - W_f) \rho_f \sigma_m^*)(W_f \rho_m + (1 - W_f) \rho_f)^{n_\sigma}}{(W_f \rho_m (1 + \alpha_{pf}) + (1 - W_f) \rho_f (1 + \alpha_{pm}))^{n_\sigma + 1}} \quad (15)$$

Region B ($W_f \geq W_{ftrans}$)

$$E_c = \frac{(W_f \rho_m V_{fmax} E_f + (1 - W_f) \rho_f V_{fmax} E_m)(W_f \rho_m V_{fmax} + (1 - W_f) \rho_f V_{fmax})^{n_E}}{(W_f \rho_m)^{n_E + 1}} \quad (16)$$

$$\sigma_{cu} = \frac{(W_f \rho_m V_{fmax} \sigma_{fu} + (1 - W_f) \rho_f V_{fmax} \sigma_m^*)(W_f \rho_m V_{fmax} + (1 - W_f) \rho_f V_{fmax})^{n_\sigma}}{(W_f \rho_m)^{n_\sigma + 1}} \quad (17)$$

In the modelling of composite mechanical properties, the fibre weight content (W_f) is set as the independent variable, and composite stiffness (E_c) and strength (σ_{cu}) are set as the dependent variables. The effective fibre stiffness (E_f) and effective fibre strength (σ_{fu}) are set as derived parameters. The values of the remaining parameters are given in Tables 1 and 2. The models are fitted to the experimental data of E_c vs. W_f and σ_{cu} vs. W_f by using non-linear regression. The goodness of fitting is evaluated by adjusted R-squared values, which has been adjusted for the number of predictors in the model from R-squared values.

3. Materials and methods

3.1. Plant material

Hemp (*Cannabis sativa* L.), variety USO-31, was sown in France (N 48.8526°, E 3.0190°(WGS84)) as described in detail in Liu et al. [5]. The whole hemp stem under the inflorescence base was used as the starting material in the present study. Hemp stem pieces with a length of approx. 15 cm were randomly collected from the stems. The hemp stems were hydrothermally pre-treated at 121 °C for 30 min in an autoclave. Hemp fibre strips were manually peeled off from the pre-treated stems, and then they were enzymatically treated by using pectinases as described in detail by Liu et al. [9]. After enzymatic treatment, the fibre strips were dried at 50 °C for 12 h. For comparison, field retting of the hemp stems was carried out for 20 days after harvest [4].

3.2. Manufacturing of composites

The treated bast fibre strips were manually untangled and aligned to allow the fibres to be processed into unidirectional composites. Bundles of fibre strips were firstly cut to a length of 140 mm, and the fibre strips were then justified to a bunch of fibre strips with masses in the range 0.6 – 2.3 g. Bunches of fibre strips were then put in the mould chambers. Afterwards, a press beam was placed on the top of the fibre strips in each chamber, and two insert beams were used to fix the height of the mould chambers to 2 mm. An epoxy resin (Araldite® LY 1568) and its amine hardener (Aradur® 3489) were mixed at a 100/28 mass ratio, and degassed in a vacuum oven. The setup for the vacuum infusion and moulding process is described in detail in the study by Liu et al. [9]. After curing for 12 h at 80 °C, the composite tensile specimens with dimensions of 140 × 10 × 2 mm were demoulded. Tabs with lengths of 50 mm were mounted on the composite specimens using epoxy resin (DP 460).

3.3. Volumetric composition

Composites with fibre weight contents (W_f) in the range 0 – 0.70 were obtained by varying the amount of fibres (m_f) in the mould chambers during manufacturing of composites. The fibre volume content (V_f) was determined by Eq.18.

$$V_f = \frac{m_f/\rho_f}{m_c/\rho_c} = \frac{m_f}{m_c} \times \frac{\rho_c}{\rho_f} \quad (18)$$

where m_c , ρ_f and ρ_c are composite mass, fibre density and composite density, respectively. When W_f was below 0.30, the composite specimens made by using the above mentioned moulding process were found to have irregular surfaces, and their thickness could not be measured accurately. For those cases, ρ_c was determined by the buoyancy method (Archimedes principle) using water as the displacement medium. When W_f was above 0.30, the composites specimens had flat surfaces, and their density (ρ_c) could be accurately calculated based on their dimensions (length, width and thickness).

The matrix volume content (V_m) was determined using Eq.19.

$$V_m = \frac{m_m/\rho_m}{m_c/\rho_c} = \frac{m_m}{m_c} \times \frac{\rho_c}{\rho_m} \quad (19)$$

where m_m is matrix mass. The porosity (V_p) was then determined using Eq.20.

$$V_p = 1 - V_f - V_m \quad (20)$$

3.4. Tensile properties of composites

For tensile testing of the composite specimens, an Instron Testing Machine 5566 with a load cell of 10 kN was used. Two extensometers were used for strain measurements, and a displacement rate of 1 mm/min (corresponding to a strain rate of 2.5 %/min) was used. Based on the measured stress-strain curves, stiffness (linear regression in the strain interval 0.05 – 0.25%), strength and failure strain was

determined. For each type of composite with the differently treated hemp fibres, at least 10 specimens with varied fibre content were tested.

4. Results and discussion

4.1. Composite volumetric composition

The fibre correlated porosity factor (α_{pf}) of the composites manufactured with the differently treated fibres is determined in Figure 1a based on the experimental values of V_p and V_f using Eq.2. The values of α_{pf} for the different fibre treatments are shown in Table 2. As shown, composites with field retted and untreated fibres have the highest porosity factor of about 0.16. In contrast, composites with the enzymatically treated fibres have a much lower porosity factor of 0.12, followed by the lowest porosity factor of 0.08 for composites with the hydrothermally pre-treated and enzymatically treated fibres.

The variation of the composite porosity factor with the different fibre treatments can be explained by the changes of the fibre microstructure. When the hemp fibre strips are subjected to pectinases, pectin in the epidermis, in the parenchyma cells, and in the middle lamella regions between fibre cells are partly hydrolysed by enzyme catalysed reactions. This degradation of pectin loosens the bonding between epidermis and cortex, between fibres and parenchyma cells, and between fibres, and consequently, the epidermis and parenchyma cells are partly removed from the hemp fibre strips. With the partly removal of epidermis and parenchyma cells, which consist of a large amount of voids, the fibre bundles are split into smaller fibre bundles [9]. All these changes to the fibre microstructure collectively contribute to the decrease of α_{pf} after the enzymatic treatment.

The transition fibre weight content ($W_{f \text{ trans}}$) for each type of fibre treatment was calculated by using Eq.1 with the obtained fibre correlated porosity factors. The values of $W_{f \text{ trans}}$ are shown in Table 2. It is found that the transition value decreases from 0.77 for composites with field retted and untreated fibres, to 0.75 for composites with enzymatically treated fibres, and finally to 0.74 for composites with hydrothermally pre-treated and enzymatically treated fibres. According to Eq.1, it is evident that the decrease of $W_{f \text{ trans}}$ with fibre processing is directly governed by the decrease of the fibre correlated porosity factor.

Experimental data on the volumetric composition in the composites with the differently treated fibres, and the corresponding model lines are shown in Figure 1b. Besides the difference in the values of $W_{f \text{ trans}}$, it is shown that composites with hydrothermally pre-treated and enzymatically treated fibres have higher fibre volume content (V_f) and matrix volume content (V_m), and lower porosity than the composites with field retted and untreated fibres at any given fibre weight content below $W_{f \text{ trans}}$. According to Eqs.3 – 5, the difference in α_{pf} explains the difference in volumetric composition between the composites. Altogether, the results in Figure 1b reveal that the full volumetric composition in composites with a given type of fibre treatment can be predicted by using the model, and by using a given fibre weight content that is used for the manufacturing of the composites as input.

Table 2. Fibre correlated porosity factor (α_{pf}) and transition fibre weight content ($W_{f \text{ trans}}$) of composites with differently treated hemp fibres.

Fibre sample	Fibre correlated porosity factor (α_{pf})	Transition fibre weight content ($W_{f \text{ trans}}$)
Field retted	0.162	0.772
Untreated	0.157	0.770
Enzymatically treated	0.119	0.753
Hydrothermally pre-treated + enzymatically treated	0.084	0.738

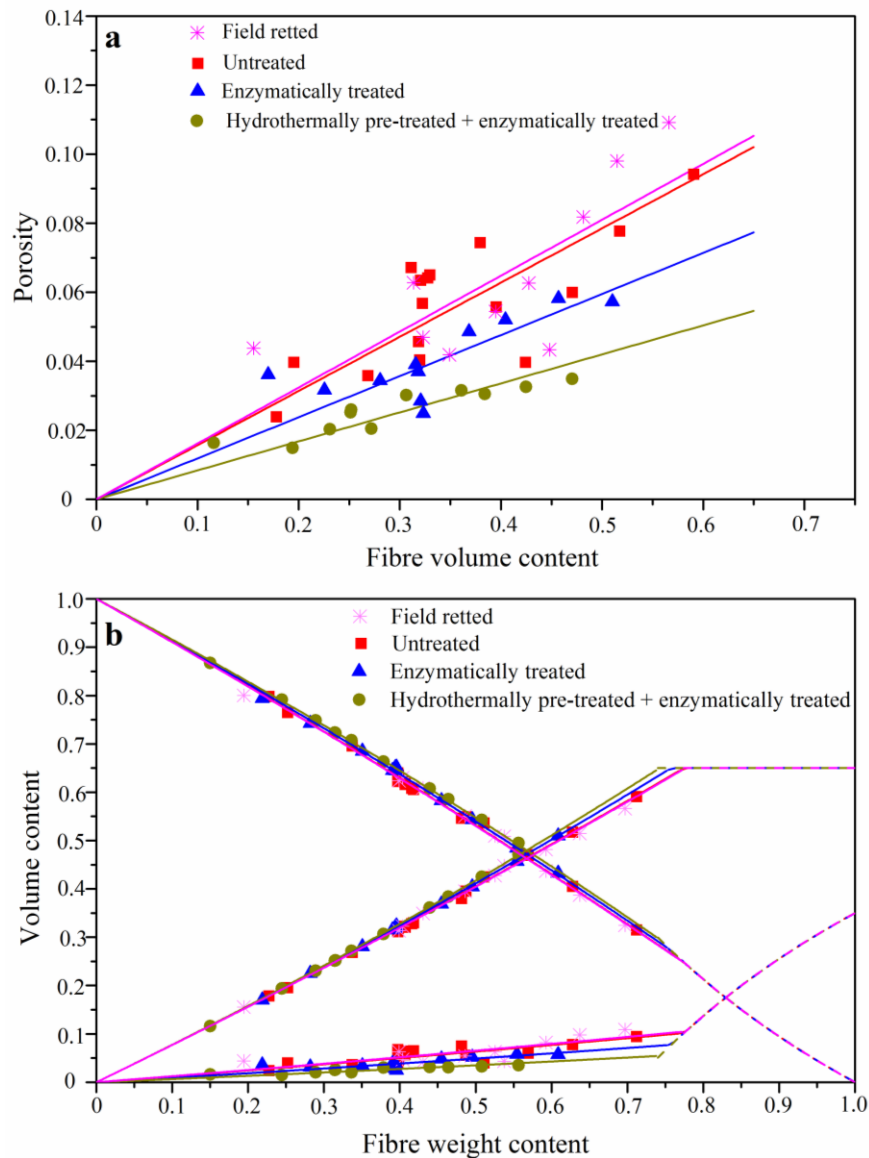


Figure 1. Composite porosity vs. fibre volume content (a), and composite volumetric composition (V_f , V_m and V_p) vs. fibre weight content (b).

4.2. Composite density

Figure 2 shows that the composites with the untreated and field retted fibres have the lowest density, which is a result of the highest porosity content and lowest fibre volume content in these composites (see Figure 1). In contrast, the composites with the enzymatically treated fibres, particularly the hydrothermally pre-treated and enzymatically treated fibres, exhibit clearly higher density due to their lower porosity contents and higher fibre volume contents. The model predictions of composite density in Figure 2 show that the predicted composite density is in good agreement with the experimental data. Therefore, the density of composites with a given type of fibre treatment can also be well predicted as a function of the fibre weight content.

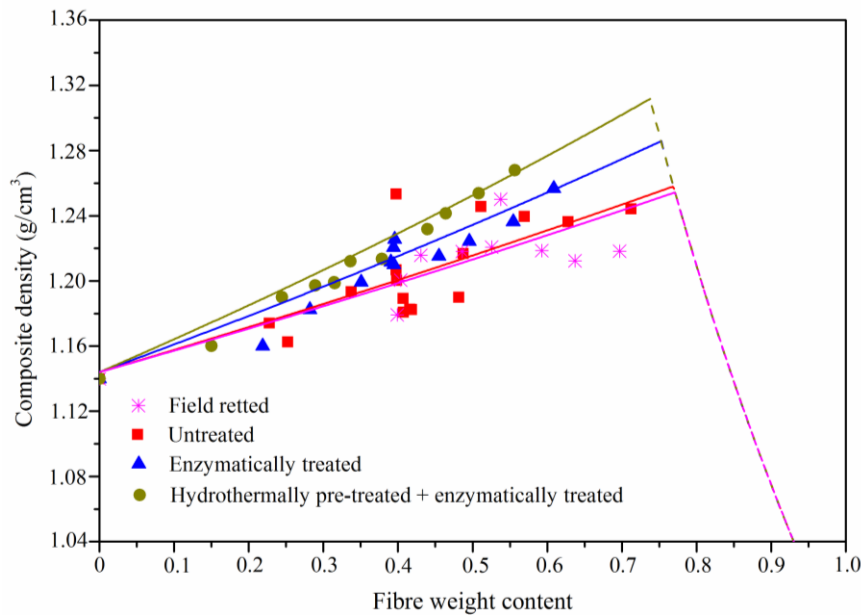


Figure 2. Composite density vs. fibre weight content.

4.3. Composite mechanical properties

In Figures 3 and 4, showing composite stiffness and strength as a function of the fibre weight content, the starting points of the model lines at $W_f = 0$ are equal to the measured epoxy matrix stiffness (E_m) of 2.7 GPa, and the epoxy matrix stress of 27 MPa at the average composite failure strain of 1.0%. Generally, the model lines are in good agreement with the experimental data.

The model lines in Figures 3 and 4 are established by setting the porosity efficiency exponent (n) equal to 0 and 2. For $n = 0$, it is assumed that all the porosity is located inside the fibres, in the so-called lumen, and this is assumed to have no effect on the mechanical properties of the composites. For $n = 2$, it is assumed that all the porosity is located outside the fibres, e.g. at the fibre/matrix interface or in the fibre bundles to produce un-impregnated fibres. This is assumed to lead to stress concentrations, which is modelled by setting n equal to 2 [14,15]. When $n = 0$, as shown in Figures 3a and 4a, composite stiffness and strength are increased non-linearly with W_f with an upward curvature until $W_{f \text{ trans}}$, and thereafter, stiffness and strength are only slightly reduced. When $n = 2$, as shown in Figures 3b and 4b, composite stiffness and strength are increased non-linearly with W_f with a downward curvature until $W_{f \text{ trans}}$, and thereafter, stiffness and strength are reduced radically. The downward curvature of the model lines is most obvious for the composites with the highest porosity content, such as the composites with the field retted and untreated fibres.

When comparing the model lines in Figures 3 and 4 for composites with the differently treated fibres, it is evident that the composites with hydrothermally pre-treated and enzymatically treated fibres have the highest stiffness and strength, followed by the composites with enzymatically treated and untreated fibres, while the composites with field retted fibres have the lowest stiffness and strength.

The fitted values of the effective fibre stiffness (E_f) and fibre strength (σ_{fu}) established by the model lines in Figures 3 and 4 are shown in Table 3. Field retted samples are found to have the lowest effective fibre stiffness of 52 and 61 GPa, and the lowest effective fibre strength of 474 and 558 MPa, when the porosity efficiency exponent is set equal to 0 and 2, respectively. There is a tendency that the effective fibre stiffness and strength increase from untreated fibres, to enzymatically treated fibres, and finally to hydrothermally pre-treated and enzymatically treated fibres, irrespective of the porosity efficiency exponent values. The hydrothermally pre-treated and enzymatically treated fibres have the

highest effective stiffness of 74 GPa and 83 GPa, and the highest effective strength of 625 MPa and 667 MPa, when porosity efficiency exponent is set equal to 0 and 2, respectively.

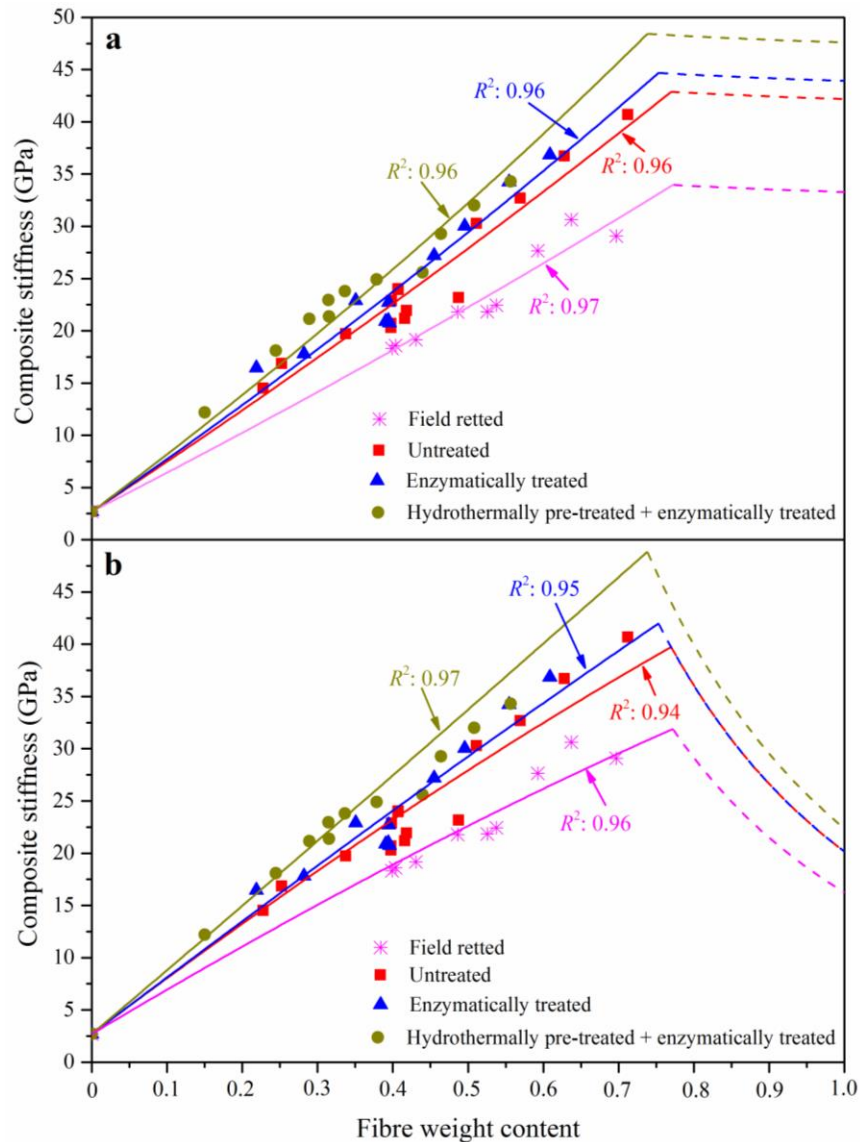


Figure 3. Composite stiffness vs. fibre weight content. Model lines are made using a porosity efficiency exponent of (a) 0 and (b) 2. Values of adjusted R-squared of fitting are shown next to the model lines.

Table 3. Established values of effective fibre stiffness (E_f) and fibre strength (σ_{fu}) in composites with differently treated hemp fibres. The porosity efficiency exponents (n_E and n_σ) are set to be either 0 or 2.

Fibre sample	E_f (GPa)		σ_{fu} (MPa)	
	$n_E=0$	$n_E=2$	$n_\sigma=0$	$n_\sigma=2$
Field retted	52	61	474	558
Untreated	65	75	569	655
Enzymatically treated	68	75	587	644
Hydrothermally pre-treated + enzymatically treated	74	83	625	667

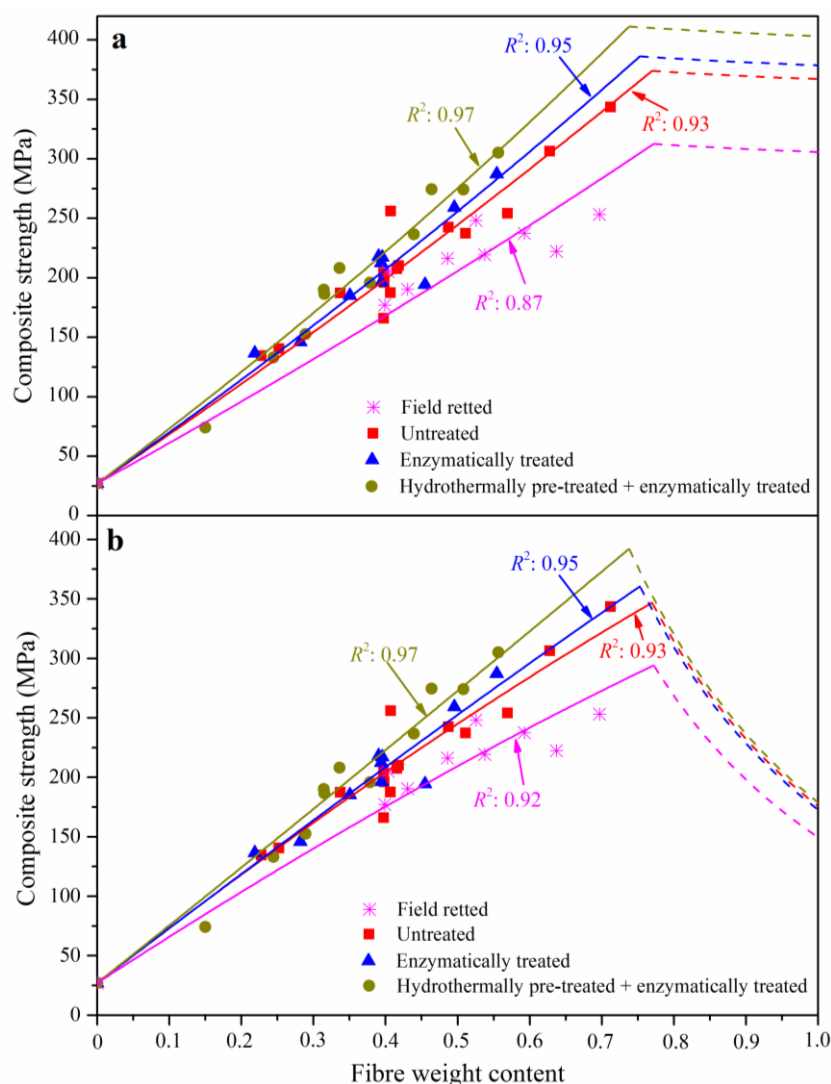


Figure 4. Composite strength vs. fibre weight content. Model lines are made using a porosity efficiency exponent of (a) 0 and (b) 2. Values of adjusted R-squared of fitting are shown next to the model lines.

5. Conclusions

Models for the volumetric composition, density and mechanical properties (i.e. stiffness and strength) of composites with differently treated hemp fibres were applied for evaluating the effect of enzymatic fibre treatments on fibre performance in composites. It is shown that the applied models are in good agreement with the experimental data. The established effective fibre stiffness and strength are used to quantify the effect of the enzymatic fibre treatments on the performance of the fibres in the composites. Altogether, the applied models are shown to be useful tools for the prediction of properties of composites with differently treated hemp fibres.

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