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VOLUMETRIC COMPOSITION OF NANOCOMPOSITES

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ABSTRACT

Detailed characterisation of the properties of composite materials with nanoscale fibres is central for the further progress in optimization of their manufacturing and properties. In the present study, a methodology for the determination and analysis of the volumetric composition of nanocomposites is presented, using cellulose/epoxy and aluminosilicate/polylactate nanocomposites as case materials. The buoyancy method is used for the accurate measurements of materials density. The accuracy of the method is determined to be high, allowing the measured nanocomposite densities to be reported with 5 significant figures. The plotting of the measured nanocomposite density as a function of the nanofibre weight content is shown to be a first good approach of assessing the porosity content of the materials. The known gravimetric composition of the nanocomposites is converted into a volumetric composition. An analytical model, previously established for conventional fibre composites, is used for the analysis of the volumetric composition. For the aluminosilicate/polylactate nanocomposites, based on the established linear relationship between the porosity content and the fibre volume content, the fibre correlated porosity factor is determined to be 0.18. Geometrical considerations of the packing of parallel nanofibres in a square array are used to make the assumption that the maximum obtainable fibre volume content in the nanocomposites will not exceed 6 % due to the small fibre spacing that restricts full matrix impregnation. The predicted volumetric composition and density of the aluminosilicate/polylactate nanocomposites is in good agreement with the experimental data. It is demonstrated that the model provides a valuable tool for the prediction and analysis of the volumetric composition of composites with nanoscale fibres.

1   INTRODUCTION

Detailed characterisation of the properties of nanocomposite materials is central for the further progress in optimization of their manufacturing and properties. The common characteristics determined in studies of nanocomposites are the nano-micro structural configuration of the materials, such as dispersion of nanofibres in the polymer matrix, and the mechanical properties, such as tensile modulus and strength. In most cases, the volumetric composition of the materials is not determined. Instead, the content of nanofibres by weight, as determined from the ingoing masses in the manufacturing process, is typically used as a materials compositional parameter in the evaluation of the measured properties. The conversion between gravimetric and volumetric composition of multiphase composite materials requires knowledge of the densities of the constituent phases, as well as the density of the composite material itself. If the latter parameter is not measured, but simply calculated, this leads to a negligence of the porosity content in the composites.

Even if the determined porosity content of nanocomposites is low, with typical values below 1%, it should be related with the similarly low volume content of nanofibres, with typical values below 5%. Moreover, when the porosity is expected to be located in vicinity to the nanofibres, it must be considered to be a critical structural parameter for the mechanical properties of the nanocomposites.

Usually, nanocomposites show an optimum in mechanical properties at a relative low weight content of nanofibres. It can be speculated that this is related to the constraints given by the geometrical packing configuration of nanoscale fibres leading to a low maximum obtainable volume content of nanofibres in composites.

2 MATERIALS AND METHODS

2.1 Cellulose/epoxy (CE) nanocomposites

Post-treatment of cellulose nanofibres was done by a two-step approach of first allylation with allyl glycidyl ether, followed by epoxidation to produce surface treated cellulose nanofibres which can be cross-linked with epoxy. A two-component solvent free epoxy was used as matrix. The aqueous cellulose nanofibres were solvent exchanged to ethanol and dispersed in epoxy resin in a 5 wt% solution, followed by solvent evaporation to produce epoxy resins with cellulose nanofibre weight contents of 0, 1.0, 1.5 and 2.0 %. The hardener was then mixed mildly with the resin paying attention not to incorporate air while mixing. For the resin with the 1.5 % nanofibre weight content, air bubbles were removed with a dispergator. Nanocomposite plates of 4 mm thickness were cast and hardened at room temperature.

2.2 Aluminosilicate/polylactate (AP) nanocomposites

Polylactate (PLA) (grade 3051D) was purchased from Nature Works IngeoTM and dried at 50 °C for 12 h prior to blending. PLA composites reinforced with 0 - 10 % weight content of aluminosilicate nanofibres (also denoted halloysite nanotubes [1]) were prepared by melt compounding in a Brabender-internal mixer. Blends were first mixed for 3 min at 30 rpm and 170 °C (during the loading of nanofibers) followed by a vigorous mixing of another 5 min at 60 rpm with applied temperature of 180 °C. Afterwards, the blends were extracted and cooled down to room temperature and then cut in to small pieces. The extracted material was subsequently compression molded into films with thickness of approximate 1 mm using a hot-hydraulic press at 180 °C (pressed for 2-5 min with pressure of 5 MPa). Finally, the samples were rapidly cooled down to room temperature in a water circulating chamber at a rate of 10 °C/min.

2.3 Density measurements

A number of methods for measurements of materials density based on small and irregularly shaped samples have been reviewed by Pratten [2]. The key challenge is to accurately determine the volume of the samples. The typically applied approach is to determine the volume via the accurate determination of mass of the sample by weighing the sample in a displacement medium, typically a liquid such as water, with known density. In the present study, the buoyancy method using water as the displacement medium is used to measure the density of the two types of nanocomposite materials. The samples of CE and AP nanocomposites were having the dimensions of 10 x 80 x 4 and 50 x 50 x 1 mm^3 (width x length x thickness), respectively.

The physical mechanism behind the buoyancy method is the existence of an upward buoyancy force of a submerged body of solid matter, where the buoyancy force is equal to the mass of the displaced liquid (Archimedes principle). The buoyancy method consists of weighings of the materials sample in air, and submerged in a displacement medium. The materials density is then calculated by the equation:

$$\rho_{sample} = \frac{m_{sample}}{v_{sample}} = \frac{m_{sample}}{\dfrac{m_{sample} - m_{sample}^*}{\rho_{disp.medium}}} = \frac{m_{sample}}{m_{sample} - m_{sample}^*} \rho_{disp.medium} \qquad (1)$$

where m^*_{sample} is the mass of the submerged materials sample.

The accuracy, or uncertainty, of the determined density ($s_{\rho_{sample}}$) for single measurements by the buoyancy method can be determined by the error propagation formula:

$$s_{\rho_{sample}} = \sqrt{\left(\frac{\partial \rho_{sample}}{\partial m_{sample}}\, s_{m_{sample}}\right)^2 + \left(\frac{\partial \rho_{sample}}{\partial \rho_{disp.medium}}\, s_{\rho_{disp.medium}}\right)^2 + \left(\frac{\partial \rho_{sample}}{\partial m^*_{sample}}\, s_{m^*_{sample}}\right)^2} = \qquad (2)$$

$$s_{\rho_{sample}} = \sqrt{\left(-\frac{m^*_{sample}\, \rho_{disp.medium}}{\left(m_{sample} - m^*_{sample}\right)^2}\, s_{m_{sample}}\right)^2 + \left(\frac{m_{sample}}{\left(m_{sample} - m^*_{sample}\right)}\, s_{\rho_{disp.medium}}\right)^2 + \left(\frac{\rho_{disp.medium}\, m_{sample}}{\left(m_{sample} - m^*_{sample}\right)^2}\, s_{m^*_{sample}}\right)^2}$$

The value of the in-going uncertainty parameters $s_{m_{sample}}$, $s_{m^*_{sample}}$, and $s_{\rho_{disp.medium}}$ are conservatively estimated to be 0.001 g, 0.001 g, and 0.0001 g/cm^3, respectively. For a specific sample of CE nanocomposite, m_{sample}, m^*_{sample} and $\rho_{disp.medium}$ were determined to be 3.979 g, 0.450 g and 0.9980 g/cm^3, respectively, giving a sample density of 1.1253 g/cm^3, and an uncertainty of 0.0003 g/cm^3. Thus, it is demonstrated that the accuracy of the buoyancy method is relative high, which in principle allows for the reporting of the measured sample densities with 5 significant figures.

For the measurements of sample density, it was decided to follow the approach of repeated measurements of a single large sample, instead of measuring several small samples a single time. In this way, the accuracy of the method could be evaluated. Between the repeated measurements, the single samples were dried under vacuum at room temperature for at least 18 hours (overnight).

3   RESULTS

The results of the measured density of the CE and AP nanocomposites are shown in Table 1. It can be observed from the repeated measurements of the single samples that the uncertainty of the measurements is in the range of 0.0001 – 0.0050 g/cm^3, except for sample AP-04 which shows a larger uncertainty of about 0.0100 g/cm^3. In general, for all the samples, the larger measured uncertainty than the calculated one for the method itself on 0.0003 g/cm^3 is probably reflecting small deviations in the dry condition of the samples between the repeated measurements. The mean value of the repeated measured densities is given with four significant figures, to allow for an uncertainty of 0.0010 g/cm^3.

Nano-composite ID	Nanofibre weight content, nominal [%]	Nanocomposite density [g/cm^3]			
		1st measurement	2nd measurement	3rd measurement	Mean
CE-00	0.0	1.1251	1.1254		1.125
CE-01	1.0	1.1286	1.1287		1.129
CE-02	1.5	1.1214	1.1209		1.121
CE-03	2.0	1.1236	1.1241		1.124
AP-00	0.0	1.2506	1.2489	1.2470	1.249
AP-01	2.5	1.2629	1.2612	1.2648	1.263
AP-02	5.0	1.2766	1.2739	1.2738	1.275
AP-03	7.5	1.2878	1.2870	1.2924	1.289
AP-04	10.0	1.3183	1.3112	1.3080	1.313

Table 1: Measured density of CE and AP nanocomposites with variable nanofibre content.

In Fig. 1, the measured density of the two types of nanocomposites is plotted as a function of the nanofibre weight content. Since the density of the nanofibres is larger than the density of the matrix, the density of the nanocomposite is expected to increase as a function of the nanofibre content. In the case of zero porosity, the relationship between composite density (ρ_c) and fibre weight content (W_f) is described by the following equation, which is valid for all composite materials:

$$\rho_c = \frac{m_f + m_m}{v_f + v_m} \quad \Rightarrow \quad \frac{1}{\rho_c} = \frac{v_f + v_m}{m_f + m_m} = \frac{v_f}{m_f} W_f + \frac{v_m}{m_m} W_m = \frac{1}{\rho_f} W_f + \frac{1}{\rho_m} W_m \quad \Rightarrow$$

$$\rho_c = \frac{\rho_f \, \rho_m}{\rho_m \, W_f + \rho_f \, W_m} = \frac{\rho_f \, \rho_m}{\rho_m \, W_f + \rho_f \left(1 - W_f\right)} \tag{3}$$

where m is absolute mass, v is absolute volume, and the subscripts f and m denote fibres and matrix, respectively. In Fig. 1, the model lines are the numerical output of Eq. (3) using density values of 1.64 and 2.54 g/cm^3 for the cellulose and the aluminosilicate nanofibres, respectively [3,4], and density values of 1.125 and 1.249 g/cm^3 for the epoxy and PLA matrix, respectively. The density values of the nanofibres represent the estimated absolute density of the bulk materials, excluding any internal pores. The density values of the matrix represent the measured density of the samples with zero nanofibre content (see Table 1).

As shown in Fig. 1a, the zero porosity line is well predicting the density of the CE nanocomposite with the lowest nanofibre weight content of 1.0 %. For the composites with the higher fibre weight contents of 1.5 and 2.0 %, the data points are clearly below the line indicating that these composites contain a relatively large porosity content. For the AP nanocomposites shown in Fig. 1b, the data points in the whole range of fibre contents from 2 – 10 % are only slightly below the line, indicating that these composites contain a relatively low porosity content. The data points of the AP nanocomposites are all following the expected trend of a linearly increased density when the fibre weight content is increased.
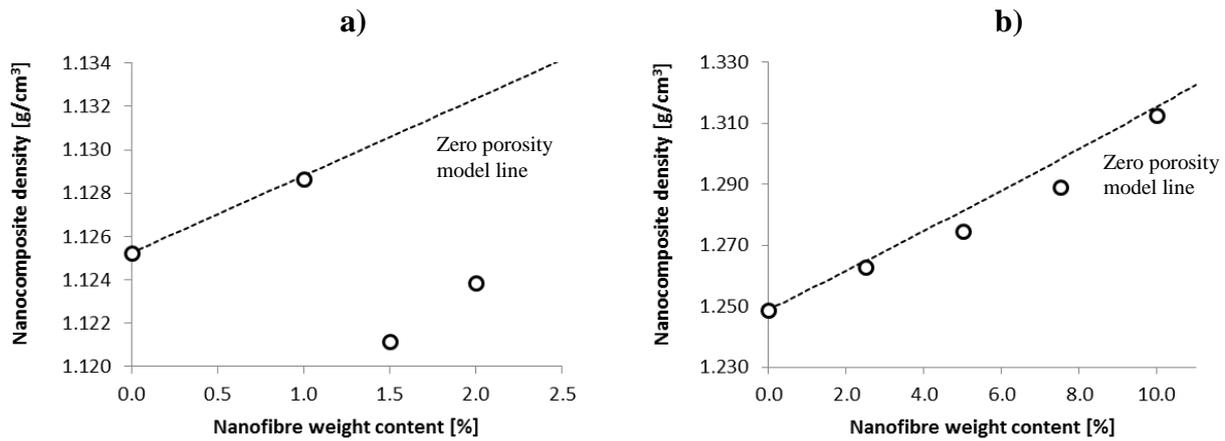
a) **b)**

Figure 1: Density of (a) CE and (b) AP nanocomposites as a function of nanofibre weight content. Data points are experimental data, and dotted lines are model predictions for materials with zero porosity.

Based on the experimental data of fibre weight content and composite density, the volumetric composition of the CE and AP nanocomposites can be calculated using the conventional equations to convert between the gravimetric and volumetric composition of composites [5]. Those results are shown in Table 2. It can be observed that the numerical difference between the weight and volume content of nanofibres is smaller for the CE nanocomposites than for the AP nanocomposites. This is due to the smaller numerical difference between the density of fibres and matrix for the CE nanocomposites compared to the AP nanocomposites (1.64 and 1.125 g/cm^3 versus 2.54 and 1.249 g/cm^3). As an example, a cellulose weight content on 2.0 % results in an only slightly lower volume content on 1.4 %, whereas an aluminosilicate weight content on 10.0 % results in a much smaller volume content on 5.2 %. This fundamental weight/volume relationship for composites needs to be recognized in the manufacturing of nanocomposites, and in the further evaluation of their properties.

Nano-composite ID	Gravimetric composition [%]		Composite density [g/cm^3]	Volumetric composition [%]		
	Nanofibres	**Matrix**		**Nanofibres**	**Matrix**	**Porosity**
CE-00	0.0	100.0	1.125	0.0	100.0	0.00
CE-01	1.0	99.0	1.129	0.7	99.3	0.00
CE-02	1.5	98.5	1.121	1.0	98.1	0.80
CE-03	2.0	98.0	1.124	1.4	97.9	0.72
AP-00	0.0	100.0	1.249	0.0	100.0	0.00
AP-01	2.5	97.5	1.263	1.2	98.6	0.16
AP-02	5.0	95.0	1.275	2.5	97.0	0.52
AP-03	7.5	92.5	1.289	3.8	95.5	0.71
AP-04	10.0	90.0	1.313	5.2	94.6	0.25

Table 2: Gravimetric and volumetric composition of CE and AP nanocomposites with variable nanofibre content.

Table 2 presents the determined porosity contents of the two nanocomposites. For the CE nanocomposites, the porosity content is 0 % for the composite with the lowest fibre content, and it is 0.8 % for the two composites with the larger fibre contents. It can be realised that for these two composites, the porosity content is almost on the same level as the fibre volume contents of 1.0 and 1.4 %. For the AP nanocomposites, the porosity content is increased from 0.2 to 0.7 % when the fibre volume content is increased from 1.2 to 3.8 %. For the composites with the highest fibre volume content on 5.2 %, the porosity content is low at 0.2 %. These determined porosity contents for the CE and AP nanocomposites correspond to the deviation of the data points from the zero porosity line in Fig. 1.

In the study by Madsen et al. [6] on conventional fibre composites, the existence of a linear relationship between the porosity content and the fibre content of the composites is proposed based on geometrical considerations. Such a linear relationship has been verified experimentally in a number of studies [6-9]. In the present study, a similar analysis will be performed for the AP nanocomposites. In Fig. 2, based on the data in Table 2 for the AP nanocomposites, the porosity content is plotted as a function of the fibre volume content. A linear regression line with intercept at the origin is fitted to the three data points of 1.2, 2.5, and 3.8 % fibre volume content. It can be observed that these three experimental data points are in good agreement with the expected linear relationship. The proportionality constant, i.e. the slope of the line, is denoted the *fibre correlated porosity factor*, and is used as an input parameter for the modelling of the volumetric composition in composites [6]. In the present case of the AP nanocomposites, the fibre correlated porosity factor (α_{pf}) is equal to 0.18.

The reason for the clearly lower porosity content on 0.2 % for the AP nanocomposite with the largest fibre volume content of 5.2 % is unknown. This sample was also showing the largest uncertainty, as mentioned above. All the AP nanocomposites were manufactured using the same manufacturing technique and with the same process conditions.

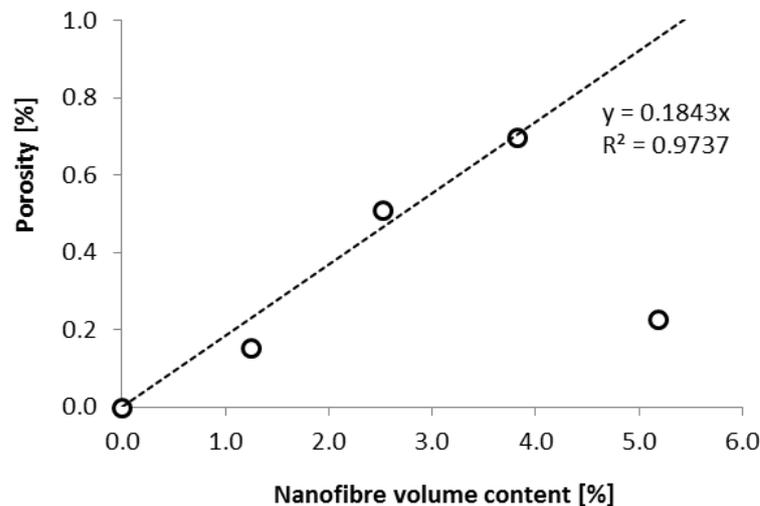$$y = 0.1843x$$
$$R^2 = 0.9737$$

Figure 2: Porosity as a function of nanofibre volume content for the AP nanocomposites. Data points are experimental data, and dotted line is a linear regression line with intercept at the origin. The deviating data point at 5.2 % is not used for the linear regression line.

Another aspect influencing the volumetric composition of composites is the geometrical packing of the fibres. For conventional microscale fibre composites, it is well recognized that there exist a *maximum obtainable fibre volume content* which depends on the packing configuration of the fibres and the applied consolidation pressure used in the manufacturing process. In the ideal case of parallel fibres organised in a square array, it can be shown that the maximum fibre volume content is 78.5 % (= 100 ¼ π). This situation is schematized in Fig. 3. The following set of equations describes the relationship between the fibre volume content (V_f), the spacing between the fibres (Λ_1 and Λ_2), and the fibre diameter (d):

$$V_f = \frac{\pi \frac{1}{4} d^2}{L^2} \quad \Rightarrow \quad L = \sqrt{\frac{\pi \frac{1}{4}}{V_f}}\, d \tag{4}$$

$$L = \Lambda_1 + d \quad ; \quad L^2 + L^2 = (\Lambda_2 + d)^2 \quad \Rightarrow \quad L = \frac{\Lambda_2 + d}{\sqrt{2}} \tag{5, 6}$$

$$\Lambda_1 + d = \sqrt{\frac{\pi \frac{1}{4}}{V_f}}\, d \quad \Rightarrow \quad \Lambda_1 = \left(\sqrt{\frac{\pi \frac{1}{4}}{V_f}} - 1\right) d \quad \Rightarrow \quad \frac{\Lambda_1}{d} + 1 = \sqrt{\frac{\pi \frac{1}{4}}{V_f}} \quad \Rightarrow \quad V_f = \frac{\pi}{4}\, \frac{1}{\left(\frac{\Lambda_1}{d} + 1\right)^2} \tag{7}$$

$$\frac{\Lambda_2 + d}{\sqrt{2}} = \sqrt{\frac{\pi \frac{1}{4}}{V_f}}\, d \quad \Rightarrow \quad \Lambda_2 = \left(\sqrt{\frac{\pi \frac{1}{2}}{V_f}} - 1\right) d \quad \Rightarrow \quad \frac{\Lambda_2}{d} + 1 = \sqrt{\frac{\pi \frac{1}{2}}{V_f}} \quad \Rightarrow \quad V_f = \frac{\pi}{2}\, \frac{1}{\left(\frac{\Lambda_2}{d} + 1\right)^2} \tag{8}$$

At L = d (i.e. maximum fibre packing)

$$\Lambda_1 = 0 \quad ; \quad \Lambda_2 = \left(\sqrt{2} - 1\right) d \quad ; \quad V_f = \pi \tfrac{1}{4}$$

Fig. 4 shows a plot of the smallest fibre spacing (Λ_1) as a function of V_f for a range of fibre diameters from 100 nm to 10,000 nm. When the fibres are maximally packed with a zero fibre spacing (Λ_1), the fibre volume content is equal to 78.5 %. This maximum packing of fibres is independent of the fibre diameter. However, it can be observed that for fibre diameters on the nanoscale below 1000 nm, to achieve large fibre volume contents implies a low fibre spacing. As an example, for fibres with a diameter of 200 nm, the achievement of a fibre volume content above 6 % implies a fibre spacing below 500 nm. It can be expected that such small fibre spacing will affect the ability of the matrix polymer to impregnate the fibres, i.e. this will form a geometrical constrain for the matrix polymer to fully impregnate the fibres. Thus, for the special case of nanoscale fibres, it can be speculated that there will exist a maximum obtainable fibre volume content governed by the limiting fibre spacing required for full matrix impregnation. Based on the presented simple geometrical considerations of a square array of fibres, the maximum obtainable fibre volume content in the AP nanocomposites with aluminosilicate fibres having diameters up to 200 nm [10], can be assumed to be about 6 %.

The above presented considerations on the existence of a maximum obtainable fibre volume content governed by the limiting spacing between nanofibres is specifically aimed at nanocomposites manufactured by a impregnation process using high viscous matrix polymers, such as the melt blending process used for the AP nanocomposites. However, the implications of a low fibre spacing are believed also to be of importance for other manufacturing techniques, such as solution casting [10,11], and in-situ polymerisation [12].
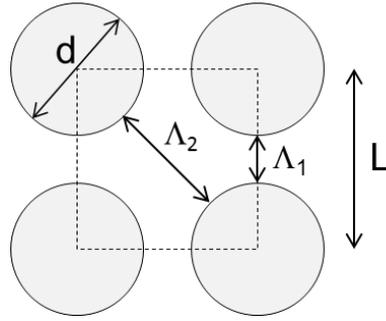
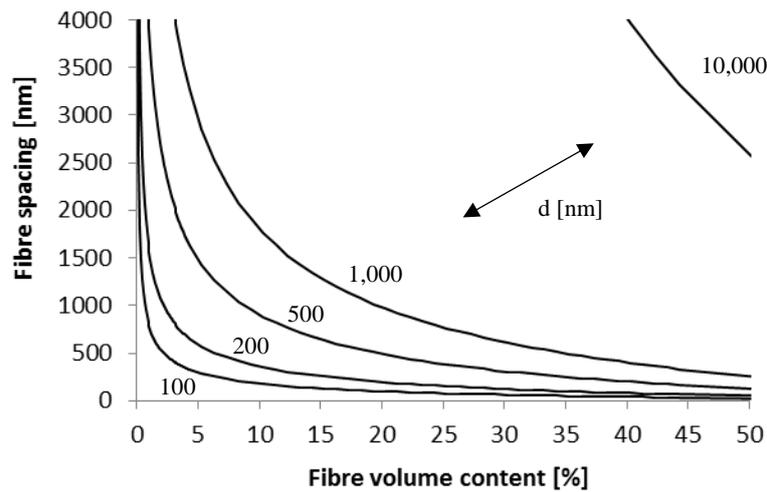Figure 3: Schematised drawing of the packing configuration of parallel fibres organised in a square array.

Figure 4: Theoretical predictions of fibre spacing (Λ_1) as a function of fibre volume content for parallel fibres packed in a square array configuration. The labels at the curves indicate fibre diameters (d) in nanometers.

A model for the volumetric composition in composites has been presented in the study by Madsen et al. [2007]. In addition to the density of the constituent fibre and matrix parts, the input parameters for the model are the fibre and matrix correlated porosity factors (α_{pf} and α_{pm}), and the maximum obtainable fibre volume content ($V_{f\,max}$). In the present study, for the AP nanocomposites, values of α_{pf} and $V_{f\,max}$ have been estimated/assumed at 0.18 and 6 %, respectively. The matrix correlated porosity factor (α_{pm}) can be set equal to zero, in accordance with the intercept of the linear regression line in Fig. 2 at the origin. Using the model equations presented in the study by Madsen et al. [2007], the volume contents of fibres, matrix and porosity can be plotted as a function of the fibre weight content. These model lines are shown in Fig. 5a for the AP nanocomposites. It can be observed that there is good agreement between the model lines and the experimental data, in the experimental range of fibre weight contents up to 10 %. At a fibre weight content of 12 %, the assumed maximum obtainable fibre volume content of 6 % is reached. If attempted to manufacture composites with a fibre weight content above this transition point of 12 %, the fibre volume content stays constant at 6 %, and instead the porosity starts to increase considerably. The underlying mechanism for this behaviour after the transition point is the reaching of a critical low fibre spacing that prevents the matrix from fully impregnating the fibres.

The density of composites, in the general case of non-zero porosity, can be calculated by the equation:

$$\rho_c = \frac{m_f + m_m}{v_f + v_m + v_p} = \frac{m_f}{v_f}\,V_f + \frac{m_m}{v_m}\,V_m = \rho_f\,V_f + \rho_m\,V_m$$

(9)

In Fig. 5b, the predicted volumetric composition is used as input in Eq. (9) to establish a plot of the composite density as a function of the fibre weight content. The model line is in good agreement with the experimental data. The large decrease of the composite density after the transition fibre weight content of 12 % is due to the concurrent large decrease of the matrix content, while the fibre content stays constant. This is equivalent to the large increase of the porosity content shown in Fig. 5a.

Altogether, it is believed that the model provides a valuable tool for the prediction and analysis of the volumetric composition of nanocomposites. The AP nanocomposites are presented as a case material to demonstrate the use of the model. Future studies are needed to verify the model for other nanocomposite systems, and to obtain better experimental data for the establishment of the input model parameters, such as the maximum fibre volume content.
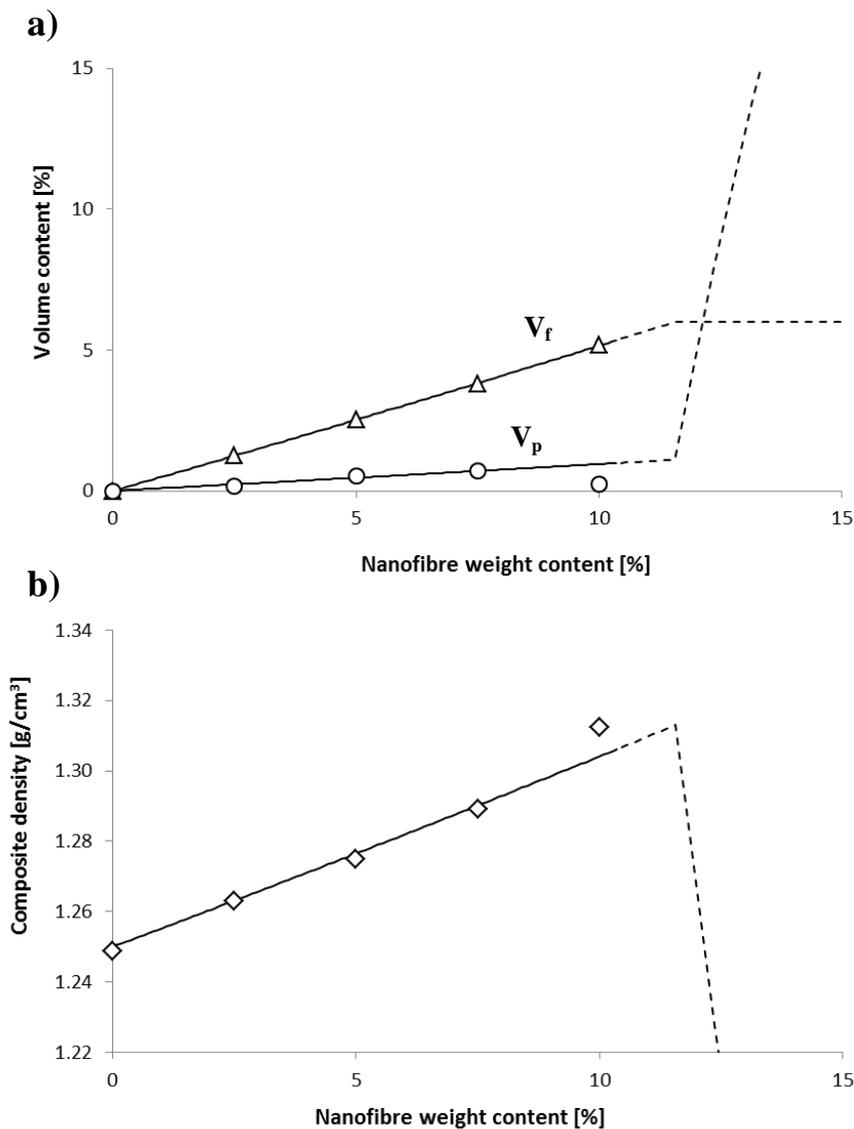
a)

b)

Figure 5: Plots of (a) volume contents of fibres and porosity, V_f and V_p, and (b) composite density as a function of nanofibre weight content for AP nanocomposites. Data points are experimental data, and lines are model predictions (solid lines inside the experimental range, dotted lines outside the experimental range).

4   CONCLUSIONS

The presented methodology for the determination and analysis of composite volumetric composition is shown to form a valuable contribution to the characterisation of properties of nanocomposites. The work has been based on two case materials: cellulose/epoxy and aluminosilicate/polylactate nanocomposites. Further studies are needed to verify the methodology for other nanocomposite systems.

ACKNOWLEDGEMENTS

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