J Mater Sci (2011) 46:3387–3398
DOI 10.1007/s10853-010-5227-4

Properties of biocomposites: influence of preparation method, testing environment and a comparison with theoretical models

M. Bulota · A. S. Jääskeläinen · J. Paltakari · M. Hughes

Received: 29 July 2010 / Accepted: 28 December 2010 / Published online: 7 January 2011

Abstract Biocomposites were prepared by solvent casting from poly(vinyl) alcohol and mechanically microfibrillated (MFC) birch pulp. Preparations varied in concentration of polymer solution, mixing time of cellulose/PVA dispersion and were either degassed or not. In addition, specimens were tested in different levels of relative humidity at a constant temperature. The results show that the preparation method has a significant influence on mechanical properties. It was observed that aggregation of microfibrills was easier at lower concentrations of polymer solution leading to inferior properties of composites. Degassing provided increase in Young's modulus and tensile strength at MFC loads below 10% (w/w). However, there was no significant change in composites density. Longer mixing time significantly deteriorated mechanical properties of biocomposites. The relative humidity proved to be very important factor. The properties of composites conditioned at 45% RH showed higher strength and stiffness properties than conditioned at 55 %RH. The experimental data were in a good agreement with percolation model.

Introduction

The reinforcement effect of fibres has been known for more than 2,000 years. Nevertheless, the mechanism of reinforcement still requires a better understanding, especially when dealing with small-scale reinforcement agents such as cellulose microfibrils. Cellulose is the most abundant biopolymer on earth, with a partially crystalline structure [1, 2] and excellent mechanical properties. These properties could be exploited as a renewable and biodegradable reinforcement agent and over the last couple decades there has been extensive work done on the disintegration of plant fibres, the isolation of cellulosic fibrils and the preparation of biocomposites from these [3–6].

So far studies on cellulose reinforced nanocomposites have focused mainly on investigating the reinforcement of different types of matrices with cellulose from different sources such as cotton [7, 8], chitin [9], sugar beet [10], sisal [11] and wood [12–16] to name but a few. There are many ways to prepare composites from the same constituents; however, the influence of the preparation method on the final mechanical properties of the composite has not been studied in detail. This is an important consideration, since the microstructure and thus the resulting micromechanics may be affected during the preparation process of the composite.

Since the overall goal of our study is to investigate the micromechanics of cellulose reinforced composites, it is important to foresee factors that might influence the mechanical properties and it was hypothesized that the preparation method might have a significant influence on the mechanical properties. Poly(vinyl) alcohol (PVA) was chosen for matrix, since it is well known and has previously been used in other studies [8, 13, 15–19]. Moreover, it is a water soluble polymer and is widely produced around the world. Poly(vinyl) alcohol (C_2H_4O)n is derived by hydrolysis from polyvinyl acetate $(C_4H_6O_2)_n$. It is an amorphous polymer with atactic chain structure, i.e. the substituent groups are randomly distributed along the chain of polymer. It can be completely dissolved at approximately 90 °C in water. The solutions are not very stable and increase in

M. Bulota (✉) · A. S. Jääskeläinen · J. Paltakari · M. Hughes
Department of Forest Products Technology, Faculty of Chemistry and Materials Sciences, School of Science and Technology, Aalto University, P.O. Box 16400, 00076 Aalto, Espoo, Finland
e-mail: mindaugas.bulota@tkk.fi

viscosity during the storage [20]. Polyvinyl alcohol does not occur as a natural material. First time, it was hydrolyzed in 1924 by Hermann and Haehnel. It is classified into fully hydrolyzed and partially hydrolyzed [21]. Solution of water and polyvinyl alcohol is transparent and forms transparent film after drying. The mechanical properties of PVA are governed by hydrogen bonding. Study by Li et al. [22] reveals that PVA exist as a supramolecular assembly stabilized by hydrogen bonds. The presence of hydroxyl groups renders the polymer hydrophilic and makes it suitable for cellulose reinforced composites due to ability to form hydrogen bonds. However, hydrophilicity renders it moisture sensitive and mechanical properties are affected due to plasticizing effect of water [23]. The combination of cellulose and PVA would yield a partially water soluble, biodegradable composite material. The use of microfibrillated cellulose (MFC) as a reinforcement agent has been widely reported in the literature [12–14, 16, 18, 24–26], even though the MFC preparation method often differs. The Young's modulus of crystalline cellulose has been reported to be around 135 GPa [27] and although a recent study by Cheng et al. [28] suggests that the Young's modulus of fibres isolated from wood might only be around half this value, the goal of harnessing natural fibres as a high performance reinforcement material continues.

Although different values for the properties of cellulosic reinforcement have been reported, dependent upon the preparation method [28], interestingly there are also wide differences reported for the properties of composites prepared from essentially the same raw materials. Lu et al. [16] studied the properties of PVA reinforced with MFC obtained from the mechanical disintegration of Kraft pulp and found that tensile strength increased by 76% and tensile modulus by 40% in comparison to pure PVA. On the other hand, Zimmerman et al. [13] reported an approximately fivefold increase in tensile strength and a two-and-a-half times increase in Young's modulus over pure PVA film in composites reinforced with MFC isolated from sulphite pulp. Although the raw materials were different, such vast differences in mechanical properties could also be attributed to the preparation methods which were different. This suggests that the reinforcement process is a very complex phenomenon and requires a deeper understanding since so many variables are involved.

Ultimately, the aim of this work is to better understand the mechanical properties of MFC reinforced polymer composites. The applicability of micromechanical models to predict these properties is therefore of great interest. The experimental data obtained in this work was ultimately compared with four theoretical models developed to predict the Young's modulus of composite materials. The first model is the classical Rule of Mixtures approach where Young's modulus is calculated according to Eq. 1.

$$E_{\mathrm{c}} = X_{\mathrm{r}}E_{\mathrm{r}} + (1 - X_{\mathrm{r}})E_{\mathrm{m}} \tag{1}$$

where E_{c} is composite modulus; E_{r} is reinforcement modulus; $E_{\mathrm{m}}$is matrix modulus; X_{r} is fibre volume fraction.

Since the advent of composite materials, predicting the final mechanical properties has been important and in the second half of a twentieth century, there were breakthroughs in the modelling of composite properties [29–34]. Modelling the properties of composites derived from polymer modelling theory where multiphase composites were hypothesized to behave like crystalline and semicrystalline polymers. The well known Halpin-Tsai equations are based on Hill's method [32, 33], who modelled composites as a single fibre embedded in a cylinder of a matrix. The Young's modulus in the case of randomly dispersed short fibres can be calculated according to Eq. 2

$$E_{\mathrm{c}} = E_{\mathrm{m}}(1 + \xi\eta X_{\mathrm{r}})/(1 - \eta X_{\mathrm{r}}) \tag{2}$$

where η is giving by

$$\eta = \frac{\mathrm{E_f/E_m} - 1}{\mathrm{E_f/E_m} + \xi} \tag{3}$$

ξ is a geometry coefficient and is calculated as following:

$$\xi = 2(l/d) \tag{4}$$

where l is fibre length, d is fibre diameter. It is hard to evaluate aspect ratio of MFC, since the fibres are of different sizes. In this study, it was assumed to be 50 GPa [15].

At the same time as Halpin and colleagues, Davies [30, 31], working in Britain, modelled the mechanical properties of composites and developed a modified rule of mixtures (Eq. 5):

$$E_{\mathrm{c}}^{n} = E_{\mathrm{r}}^{n}X_{\mathrm{r}} + E_{\mathrm{m}}^{n}X_{\mathrm{m}} \tag{5}$$

Davies suggested that the constant n be set to 1/5 based on theoretical analysis [31, 35].

Another approach yields the percolation model which has gained a lot of interest in recent decades and has been reported by many scholars as a phenomenon defining the final properties of composite materials [8, 11, 13, 16, 36–38]. The percolation theory applied to composites was recently developed by Ouali et al. [39] and assumes interactions between fibres, however, the roots of percolation theory date back to World War II. The theory is based on the assumption that chemical bonds are formed randomly. Neighbouring particles which are linked by bonds form clusters [40]. From percolation theory, Young's modulus expressed as shown in Eq. 6.

$$E_{\mathrm{c}} = \frac{(1 - 2\psi + X_{\mathrm{r}})E_{\mathrm{m}}E_{\mathrm{r}} + (1 - X_{\mathrm{r}})\psi E_{\mathrm{r}}^{2}}{(1 - X_{\mathrm{r}})E_{\mathrm{r}} + (X_{\mathrm{r}} - \psi)\mathrm{E_m}} \tag{6}$$

where ψ is a percolation volume fraction and given by:

$$\psi = X_{\mathrm{r}} \left(\frac{X_{\mathrm{r}} - X_{\mathrm{c}}}{1 - X_{\mathrm{c}}} \right)^{\mathrm{b}} \tag{7}$$

where X_c is a percolation threshold (in this work it was assumed to be 5%, since the test results did not show reinforcement below this value). Young's modulus was assumed to be 50 GPa. According to a study by Cheng et al. [28] the modulus of mechanically disintegrated fibres decreases as size increases. The modulus of commercially available MFC was reported to be 84 ± 13 GPa at a diameter of around 180 nm [28]. In this work, where the fibrils had diameter in micrometers, modulus was assumed to be lower than this and a value of 50 GPa was chosen.

The aim of this work reported herein was twofold. First to investigate the influence of composite preparation method and testing environment on the mechanical properties of PVA composite reinforced with MFC, and secondly to compare the experimental data with the aforementioned theoretical models.

Experimental section

Materials

Microfibrillated cellulose

Microfibrillated cellulose was prepared from never dried, chemically unmodified birch wood pulp. The pulp was a commercial Elemental Chlorine Free ECF[1]-bleached birch Kraft pulp. The pulp suspension was diluted to 3% consistency and cellulose microfibrils were disintegrated by using an ultra-fine friction grinder (Masuko Supermass-colloider, model MKZA 10–15 J). Silicon carbide (SiC) grinding stones were used in the refining. The gap was adjusted to 100 μm. During grinding the power consumption was maintained at between 3.2 and 3.8 kW. The pulp suspension passed five times through the grinder. The suspension was in the form of a gel and had solids content of approximately 2% (w/w).

Matrix

Poly(vinyl) alcohol (PVA) was provided by DuPont, Finland. Two types of PVA were used. The first, commercially known as Elvanol 71-30, was a fully hydrolyzed polymer with an average molecular weight (M_w) of ≈93700. The second, Elvanol 75-15, was a hydrolyzed copolymer of poly(vinyl) alcohol and methyl methacrylate (MMA) with an average M_w of ≈65500.

Methods

Composites preparation

The PVA (Elvanol 71-30) was dissolved in distilled water at +80 ± 5 °C using constant agitation by a magnetic stirrer for 1 h. It was then left to cool down for around 30 min whilst being stirred. The MFC gel was added when the solution had reached a temperature of +35 ± 5 °C. Three different concentrations of PVA solution were used: 1, 2 and 4%. Composites prepared from these three concentrations were denoted A, B and C respectively.

Composite films were made using three methods. These are summarized in Table 1. In Method 1, a dispersion of MFC in the PVA solutions was directly cast onto a glass plate and left for at least 22 h in ambient conditions and then dried in an oven at 70 ± 5 °C without air convection for 6 (solution C), 12 (solution B) and 24 h (solution A). The resulting composites were labelled A1, B1 and C1. In Method 2, the MFC in PVA solution was degassed under vacuum for at least 45 min to remove any trapped air bubbles. The casting and curing procedure described in Method 1 was then followed. Composites made in this way were labelled C2. In Method 3, the casted dispersion was degassed under vacuum for 20 h and then dried in an oven for 6 h at 70 ±5 °C. The composites were labelled B3.

Polymer PVA (75-15) was used to investigate the influence of mixing time on the mechanical properties of composites. The procedure followed the preparation method described for composite C1. The mixing times were 2 and 24 h.

Mechanical testing

Specimens for tensile test were prepared in accordance with ISO 527:1996. Specimen type 1BA was chosen, since the size of composites was limited. The specimens were punched out of the films using a custom made cutting die. There were at least five specimens in each group. The thickness of films was up to 100 μm. Specimens were conditioned in accordance with EN ISO 291:2008 at +23 ± 1 °C and 50 ± 2% relative humidity (RH) before the testing. Testing was conducted on an MTS 400/M

Table 1 Summary of the composite preparation methods

Solution concentration % (w/w)	No degassing	Dispersion degassed for 45 min in a beaker	Cast solution degassed for 20 h
1	A1	–	–
2	B1	–	B3
4	C1	C2	–

---

[1] Elemental chlorine free—bleaching without chlorine gas or hypochlorite, but chlorine dioxide (ClO2) is used in one or more stages.

testing machine situated in the same controlled environment. In the study on the effect of RH on the mechanical properties, the specimens were conditioned at 45 ± 1%RH, 50 ± 1%RH and 55 ± 1%RH for at least 72 h prior to testing.

Density measurements

The density of films was measured by cutting either 10 or 5 mm diameter discs from the composite film. The specimens were conditioned at +23 °C and 50 %RH for at least 72 h. At least five samples for each type of composite were evaluated. Sample thickness was measured with a micrometer to an accuracy of 0.01 mm (Lorentzen & Wettre SE 51 D2). Weight was recorded to an accuracy of five decimal places (Mettler Toledo AB135-S/Fact). Density was calculated according to Eq. 8.

$$\rho = \frac{\mathrm{m}}{\mathrm{V}} \tag{8}$$

where ρ is density, m is weight of a sample, and V is volume of a sample.

Scanning electron microscope (SEM) imaging

Fractured specimens were gold sputtered in a BAL-TEC SCD 050 sputter coater at 40 mA current for 15 s. Then the cross sections were imaged in a Hitachi TM-1000 table top SEM.

Viscosity measurements

Viscosity of PVA water solutions was measured using capillary viscometer in a room temperature.

pH measurements

Measurements of pH of PVA water solutions were done with Metrohm 744 pH meter.

Statistical analysis

Analysis of variance was performed in order to compare means at a significance level of 0.05. Tukey's test was employed to compare the means.

Results and discussion

Characterization of microfibrillated cellulose

MFC was a mixture of nano-sized and micro-sized fibrils. Thus the evaluation of fibril dimensions is rather difficult. Nevertheless, the length and diameter of fibrils were measured to be approximately 200 and 4 μm, respectively, from polarized light micrographs of diluted MFC water suspensions. Although, the aforementioned values refer to bundles rather than to single fibrils as SEM micrograph, Fig. 1, of MFC indicates, the estimation is reasonable since fibrils tend to aggregate in water based suspensions upon drying.

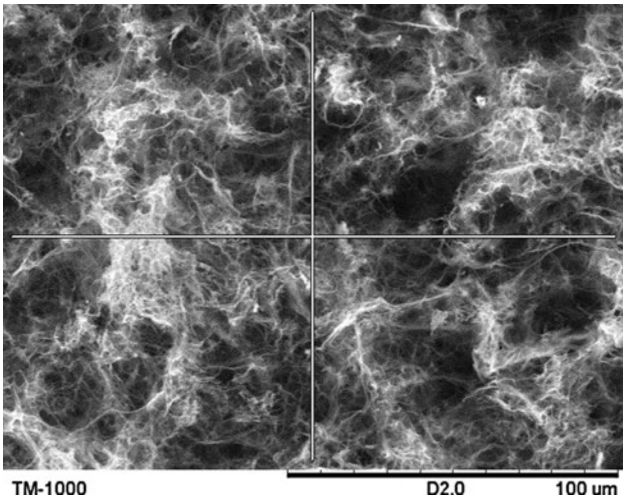

Fig. 1 SEM micrograph of MFC

The interaction of fibrils are governed by hydrogen bonding, thus a web-like structure is formed. The SEM micrograph was taken during the drying of MFC suspension in vacuum chamber, therefore, aggregation of fibrils took place to some extent. There are no other studies on composites done with the material used, however it can be seen that it consist of fine fibrils similar to what has been reported in other studies [13, 15, 16, 26]. Even though slightly different techniques were used in preparation of MFC in aforementioned studies, they share common features: the raw material is wood pulp; mechanical disintegration was employed and no chemical treatment was used. Thus, they are similar to the preparation method described herein.

Effect of concentration

The concentration of polymer solution could be a factor affecting the mechanical properties of the composites. Images of cast MFC/PVA dispersions are presented in Fig. 2. The amount of reinforcement agent is the same in all of the dispersions [1% (w/w)]. However, the concentrations of the solutions are different.

Immediately after casting, all dispersions looked similar. Aggregation of MFC started approximately 2 h after casting. The largest aggregates were formed at 1% solution concentration. In fact, the MFC formed large lumps by the

Fig. 2 Cast dispersions of MFC and PVA solution after at least 2 h under ambient conditions. The MFC load in all of the dispersions is 1%. The PVA solution concentrations are: **a** 1 %; **b** 2 % **c** 4 %

end of the curing process; therefore, it was not possible to prepare composites suitable for mechanical testing at 1% solution concentration and 1% MFC loading. Aggregates were still visible at 2% solution concentration, but were significantly smaller. A 4% solution concentration visibly prevented aggregation. This clearly indicates that simply by controlling the amount of water in the dispersion it is possible to prevent aggregation of MFC. The mobility of MFC as well as polymer chains may be limited at higher concentrations due to higher viscosity.

The influence of concentration on microfibrils dispersion implies that the mechanical properties of the composites could be affected. A comparison of the mechanical properties of the composites prepared from different solution concentrations and MFC loads is presented in Fig. 3.

As may be seen, the Young's modulus does not differ significantly between composites B1 and C1 for pure PVA film and at 1% load. Composite C1 has significantly higher modulus at 5% (w/w) MFC load. Meanwhile the Young's modulus of the A1 composite is the highest at 10% (w/w) MFC load. There are no differences between the tensile strengths of composite B1 at MFC loadings below 10%. Composite A1 exhibited the lowest tensile strength as well as Young's modulus at 5% (w/w) MFC load. This is probably due to the aforementioned aggregation of MFC. Nevertheless, the tensile strength of A1 increases at 10% (w/w) load and is equal to the strengths of the composites B1 and C1. Moreover, the Young's modulus of composite A1 exhibited the highest value at 10 and 15% (w/w) MFC load with a confidence of 95% ($\alpha = 0.05$). This can be attributed to an increase in viscosity at higher MFC loadings, consequently the dispersion of fibrils is limited. The preparation of composite C1 with 15% (w/w) MFC load was not possible due to the high viscosity of the dispersion. Clearly, insufficient dispersion of MFC severely affects the mechanical properties of the composites. The highest modulus was obtained at a solution concentration of 4 up to 5% (w/w) of MFC load. When more than 5% (w/w) of reinforcement agent is added the highest modulus is obtained at a 1% solution concentration and the 4% concentration exhibits the lowest value. The stiffness of the composites and the reinforcement phenomenon is related to the dispersion of MFC. Dispersion was hindered at higher MFC loads due to the viscosity of the dispersion. Reinforcement effects were evident at 5% (w/w) load of MFC as well as an observed increase in the dispersion viscosity, implying that the percolation phenomenon takes place at approx. 5% (w/w) load of reinforcement agent. As has been reported by number of authors, the percolation phenomenon is important in the process of reinforcement [11, 13, 15–17, 36, 37]. When MFC is used as reinforcement, the network most probably cannot be formed at low contents of reinforcement. As Zimmermann [13] suggests, a higher percolation threshold is required to obtain network formation with MFC than, for example, with nano whiskers. The reinforcing effect of MFC is a result of the interaction of fibre and polymer as well as the formation of a rigid web-like structure. The fracture surface illustrated in Fig. 4, shows the structure formed in composite by MFC.

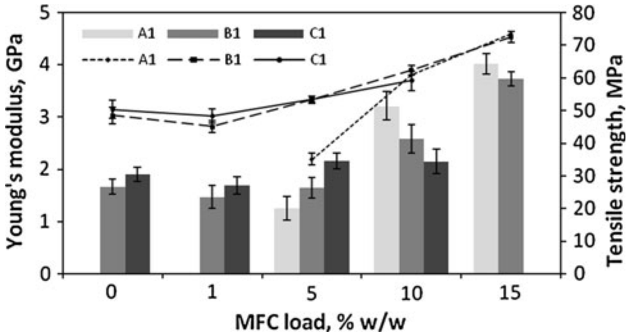

Fig. 3 Influence of solution concentration and MFC loading on mechanical properties. Columns represent Young's modulus; *curves* tensile strength. Standard deviation is depicted by *error bars*. *A1* 1% solution concentration; *B1* 2% solution concentration; *C1* 4% solution concentration

As reported in number of studies [16, 36–38], the improvement in mechanical properties is greater when the temperature is higher than the glass transition temperature (T_g) of the matrix. Aggregation of MFC takes place at higher reinforcement loadings and the network structure becomes clustered. As a result modulus and tensile strength decrease [13, 15–17].

The improvement in mechanical properties is observed in all types of composites. However the magnitude depends

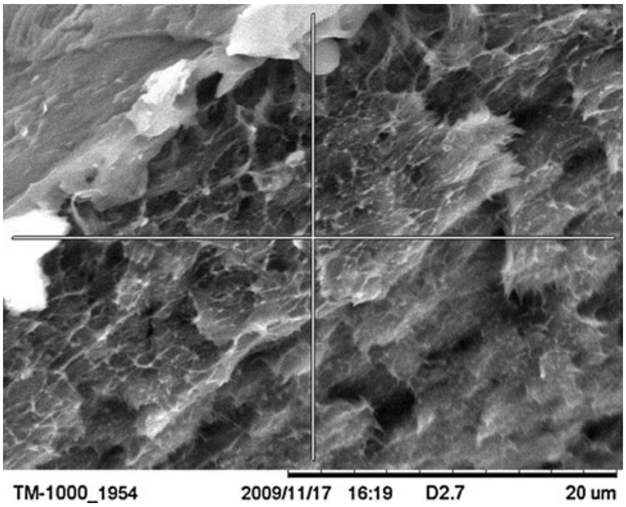

Fig. 4 SEM micrograph of a fracture surface. Cross-section of PVA/MFC composite [20 % (w/w) MFC load]

on the preparation method. The data is summarized in Table 2.

The greatest reinforcement was observed in composite type A1 (1% PVA concentration) and C1 (2% PVA concentration). However, the A1 type composites exhibited inferior mechanical properties at MFC loads of up to 5% (w/w) in comparison to B1 and C1. There was no significant difference in the mechanical properties of pure PVA with respect to PVA concentration in solution, therefore the properties of A1 composite were assumed to be equal to that of composite B1. An approximately twofold increase in Young's modulus and an increase in tensile strength of 50% were achieved at 15% (w/w) loading, whereas the Young's modulus of composite type C1 was increased by 16% and tensile strength by 20% at 10% (w/w) MFC load. The results agree well with the data in the literature [13, 16] where significant reinforcement was obtained at reinforcement contents of approximately 10% and no significant reinforcement was observed at 5% (w/w) MFC load or below. However, Chakraborty et al. [15] observed significant increases in Young's modulus already at 5% load of reinforcement agent. However microfibers, prepared from softwood kraft pulp, were used which did not form a web-like structure and were larger in size.

The work of fracture (expressed as the tensile energy absorbed over a cross-section of a sample) was affected significantly by the addition of cellulose microfibrils (Table 1). In the case of composites A1, the work of fracture was significantly reduced at 5% (w/w) and did not change significantly at higher MFC loads. It is different from the behaviour of composite B1 and C1, when a slight decrease in the work of fracture at 1% (w/w) was followed by slight increase at 5% (w/w) finally giving no change in comparison to pure PVA film. This corresponds with the trend in the tensile strength and stiffness (Young's modulus). Similarly, the work of fracture of composite B1 decreases by approximately 60 at 10% (w/w) MFC load as the modulus and tensile strength significantly improved. In the case of composite C1, the work of fracture is diminished by around 30 at 10% (w/w) MFC load, which as well corresponds to no changes in Young's modulus and decreased break strain. As can be see from Table 1 and Fig. 5, the addition of MFC yielded stronger and stiffer composites but toughness (measured as work of fracture) was reduced in comparison to pure PVA film.

The strain at break of composites A1 and B1 decreased at 10% (w/w) MFC load by approximately 80%. Meanwhile, it decreased by 52% in case of composite C1. Composites A1 and B1 exhibited similar behaviour at MFC

Table 2 Mechanical properties of composites

Composite type	MFC load (%)	Tensile strength (MPa)		Breaking strain %		Young's modulus (GPa)		Yield strength (MPa)		Work of fracture (kJ/m^2)	
		Avg	SD	Avg	SD	Avg	SD	Avg	SD	Avg	SD
A1	5	35.0	2.0	41.4	9.2	1.2	0.2	7.8	1.4	693.4	188.0
	10	60.8	2.1	20.6	5.3	3.2	0.3	21.1	2.8	617.2	182.1
	15	73.4	1.8	16.2	1.6	4.0	0.2	25.2	2.0	567.5	54.0
B1	0	48.4	2.5	149.1	46.4	1.7	0.1	12.8	1.8	3363.9	1003.9
	1	45.0	1.9	108.6	12.0	1.5	0.2	10.2	0.7	2331.5	328.1
	5	53.3	0.9	97.9	14.9	1.6	0.2	9.7	1.5	2557.2	451.2
	10	62.3	1.4	32.0	6.9	2.6	0.3	16.3	2.2	972.7	236.3
	15	72.4	1.7	21.8	2.0	3.7	0.1	23.5	3.3	767.3	84.3
C1	0	50.3	2.7	127.8	24.8	1.9	0.1	9.5	1.7	3055.4	744.6
	1	48.2	2.2	109.9	25.3	1.7	0.2	10.7	2.1	2571.3	674.7
	5	53.2	1.1	97.5	10.3	2.2	0.1	11.2	2.0	2583.0	313.0
	10	59.1	3.0	61.8	13.1	2.1	0.2	11.7	1.3	1782.4	425.4

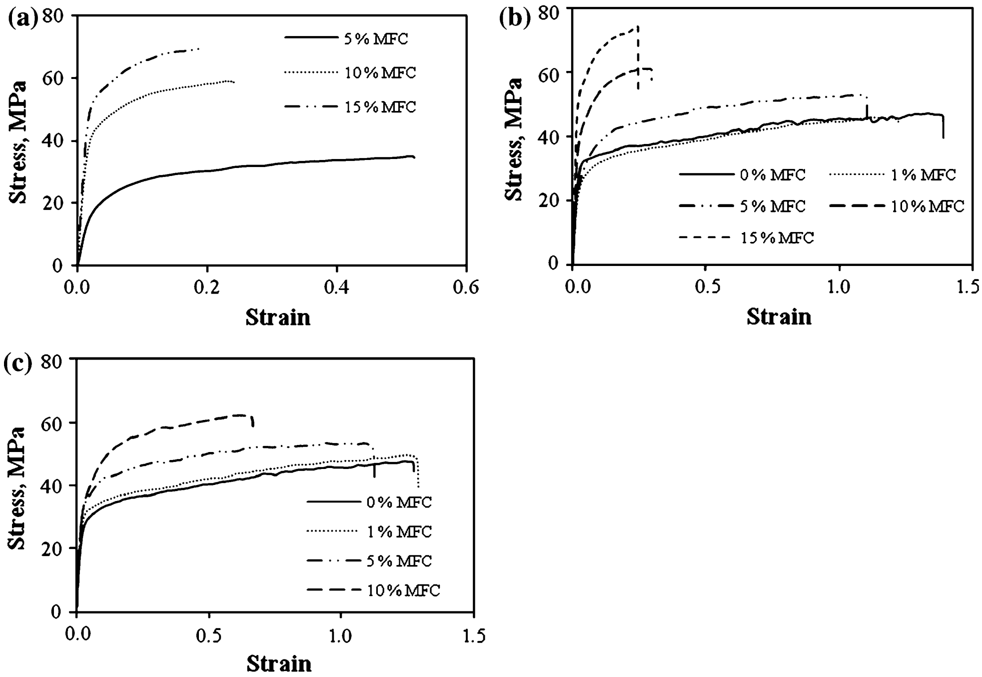

Fig. 5 Stress vs. Strain representative curves of different composite types: **a** composite A1; **b** composite B1; **c** composite C1

loads over 10% (w/w). Composite C1 had a higher toughness at 10% (w/w) MFC load due to a higher strain at break. Strain at break of composite A1 was lower, due to a much lower tensile strength—35.0 MPa as against 53.3 MPa for composite B1.

Effect of degassing

In the preparation of composite films, the formation of bubbles is often a problem. Degassing is often used to remove air from the dispersion. Composite B1 (2% solution concentration) was used to study the effect of degassing, since it showed optimal mechanical properties. The effect of degassing on the mechanical properties of the composites is presented in Fig. 6.

The Young's modulus of degassed (B3) and non-degassed (B1) composite films was found to be different. The stiffness of pure PVA film was increased by the application of vacuum. The Young's modulus was significantly different at all fibre loads except at 10% (w/w) load. Meanwhile the tensile strength was not different up to 10% (w/w) MFC load. At MFC loading over 10% (w/w), degassing decreased both Young's modulus and tensile strength. The increase of modulus at lower fibre contents theoretically could be assigned to an increase in density (see below).

Composite type C (solution concentration 4%) was also used to investigate the degassing effect, Fig. 7.

As may be seen, degassing had no significant effect on the Young's modulus. The tensile strength at 10% (w/w) load of MFC is higher if degassing is not applied. It seems that the high viscosity of the dispersion leads to limited removal of air leading to consequent clustering of micro-bubbles and finally to reduced Young's modulus.

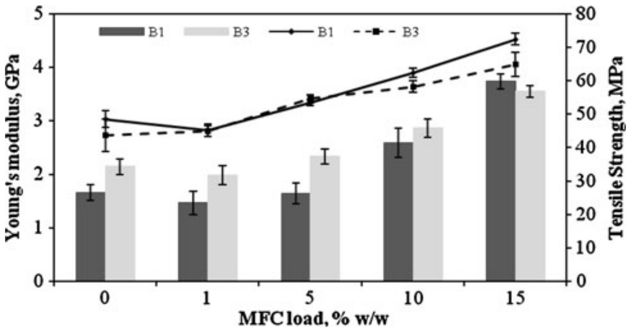

Fig. 6 The effect of degassing on composite mechanical properties. *B1* non degassed; *B3* degassed. *Columns* represent Young's modulus, *curves* tensile strength

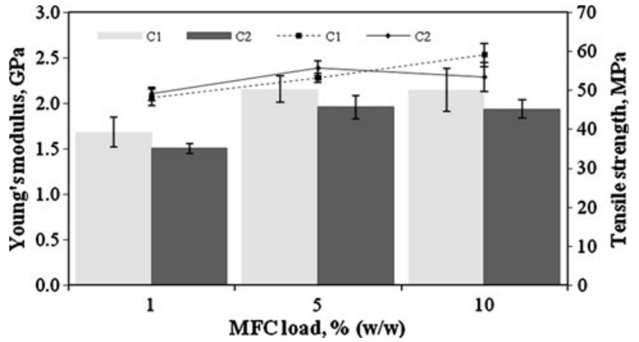

Fig. 7 The study of degassing effect on composite mechanical properties. *C1* non degassed; *C2* degassed

Effect of degassing on density

Since there was no significant influence on the mechanical properties at 4% solution concentration, the density studies were continued at 2% concentration, i.e. composite type B1 and B3, Fig. 8.

Degassing appeared to have no effect on the density of composites filled with MFC; however the density of pure PVA film was significantly increased. Overall density increases up to 5% (w/w) MFC load and then plateaus. This seems to be related to the percolation effect, which was observed to take place at 5% (w/w) MFC load. Over the percolation threshold, addition of microfibrils tends to contribute to incremental film thickness increase, rather than to density increases. To evaluate the influence of the density on the mechanical properties of the composite, specific modulus is introduced, Fig. 9. Specific modulus in this case is the Young's modulus divided by the density of the composite.

There is no difference between specific modulus of pure PVA films implying that the reason behind the increase of Young's modulus was an increase in the density. However, in case of the composites the density is not the reason for differences in changes in the mechanical properties. As noted degassing had a positive effect below MFC loads of 10% (w/w). It seems that air movement in the dispersion affect the microfibril arrangement. The micro bubbles during the travel throw the thickness of film pushes away fibrils. They can rearrange themselves at lower viscosity, due to higher mobility. However, the rearrangement is somewhat limited at higher viscosity (more MFC) affecting dispersion and leading to a loss in mechanical properties. In addition, due to high viscosity, micro-bubble may start moving in a film but stuck in other layer and distort dispersion as well as fibre–fibre interaction.

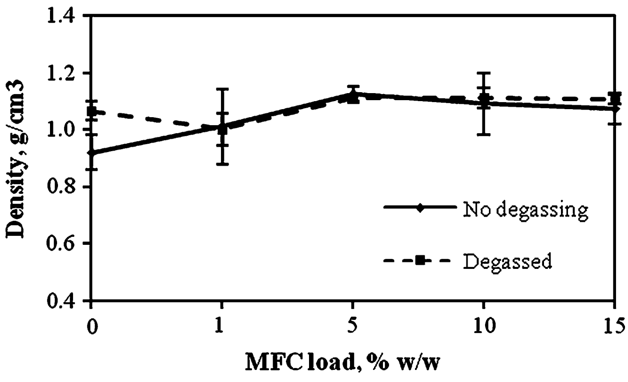

Fig. 8 Effect of degassing on composite density

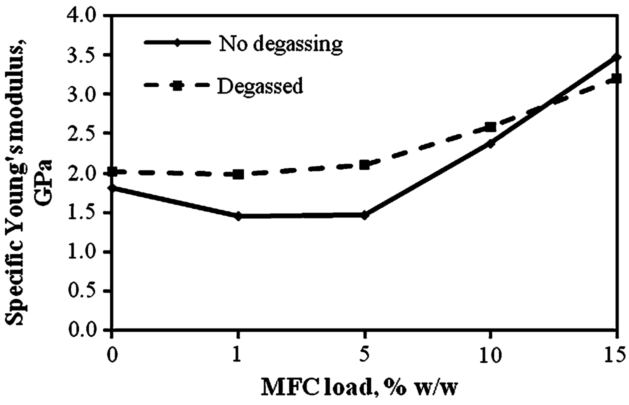

Fig. 9 Influence of degassing on specific modulus of composite

Mixing time

The effect of mixing time (2 and 24 h) of the PVA/MFC dispersion before casting is shown in Fig. 10.

As may be seen Young's modulus as well as tensile strength of pure PVA film decreased by approx. 16% as the mixing time was extended from 2 to 24 h. A drop in Young's modulus of around 42% was observed in the composites following extended mixing, while tensile strength decreased by approx. 15%. Lu et al. [16] used 24 h mixing time and reported a 40% increase in Young's modulus at 10% (w/w) MFC load. This is much lower in comparison to our result (over 100%) or that of Zimmermann et al. [13] (over 200%). Deformation of polymers is complex, since it consists of several actions occurring at the same time, namely polymer chain extension, slippage and breakage [41]. The decrease in mechanical properties could indicate degradation of the polymer. The breakage of polymer chain would lead to decrease in viscosity [42]. However, viscosity measurements with capillary viscometer did not show significant change in viscosity with respect to mixing time. Heating of PVA leads to elimination of hydroxyl and acetate groups which in turn forms acetic acid [43]. However dissolution temperature (+80 ± 5 °C) of PVA in water is not sufficient in order to cleave the side groups as pH measurements reveal. It was

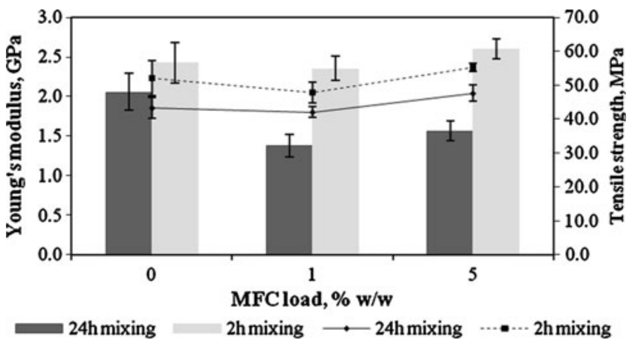

Fig. 10 Comparison of mechanical properties with respect to mixing time. Columns represent Young's modulus; *curves* tensile strength

observed that pH of the PVA/water solution was approx. 6.0 at 25 °C. The deterioration of mechanical properties of pure PVA film with respect to longer agitation time requires deeper study in order to provide elucidation. Results of viscosity and pH measurements would imply that the decrease in mechanical properties could be related to actual process rather than to changes in polymer. Dust particles and other contaminants which are present in the air are trapped in the solution and act as nucleation agents [41] which in turn could act as stress concentrators when film is loaded. Obviously, in longer mixing time the solution is exposed to contaminants for longer, therefore, the amount of nuclei would be higher. However, the polarized light microscopy did not reveal a presence of nuclei, indicating that they are, if any, below the size of 1 micrometer.

Testing environment effect on mechanical properties

The testing of composite films is normally done following standard ISO 527 or equivalent American standard ASTM D1708. In this study, ISO 527l, which describes testing of plastics and composite materials, was followed. The standard atmosphere for non-tropical countries is considered to be +23 °C and 50% relative humidity (RH). According to standard atmosphere class 1, the permitted deviation is ±1 centigrade in temperature and ±5% in relative humidity. It is known that poly(vinyl) alcohol is a hydrophilic polymer and its properties are strongly affected by the presence of water [8]. Herein, additional to the effect of the preparation method, the influence of relative humidity level within the permitted level on the mechanical properties of PVA/MFC composites was investigated. Composite type B3 was chosen for the investigation. The samples were conditioned in the aforementioned relative humidity conditions before the testing. Since the testing was done immediately after the samples had been removed from conditioning container, it is assumed that no significant changes took place in the equilibrium moisture content of the composites during testing. All the mechanical properties, except work of fracture, were affected when the environment was varied from 45 towards 55 %RH (Table 3). The tensile strength of pure PVA film decreased by 20 at 55% relative humidity, Fig. 11. The difference in tensile strength of samples tested at 45 and 55 %RH was slightly smaller and fluctuated around 14% implying that the addition of cellulose somewhat cancelled effect of different environments.

The Young's modulus of the films seems to be affected the most by different conditions, Fig. 12, with the Young's modulus of pure film decreasing by 60% between 45 and 55 %RH. The difference is moderated when the load of MFC is over the percolation threshold, i.e. 5% (w/w). The difference in Young's modulus between 45 and 50 %RH is approximately 40%, whereas difference between 50 and 55 %RH is around 25%.

A summary of the mechanical properties of composites tested in different environments is presented in Table 3.

The toughness of composites changes as MFC is added. PVA itself is a tough material and loads of MFC over 5% (w/w) decreases the toughness. There is no significant difference in toughness below 5% (w/w). Composites with 5% (w/w) MFC load are optimal if toughness, strength and

Table 3 Mechanical properties of composites tested at different levels of relative humidity

Relative humidity (%)	MFC load (%)	Tensile strength (MPa)		Strain at break (%)		Young's modulus (GPa)		Yield strength (MPa)		Work of fracture (kJ/m^2)	
		Avg	SD	Avg	SD	Avg	SD	Avg	SD	Avg	SD
45	0	54.6	5.2	88.9	4.5	3.8	0.1	26.0	5.4	2232.1	577.2
	1	50.6	3.1	82.9	12.7	3.3	0.3	23.2	1.1	1757.1	759.3
	5	60.7	1.3	72.3	5.8	4.3	0.1	23.7	3.2	2283.3	219.8
	10	67.4	0.9	20.2	10.3	4.7	0.2	28.8	2.0	713.0	384.4
	15	68.5	2.7	3.7	1.6	4.9	0.2	30.7	3.9	110.1	63.2
50	0	45.4	3.1	103.7	30.0	2.1	0.2	10.3	1.5	2300.6	760.1
	1	44.8	1.6	101.0	16.1	2.0	0.2	12.0	2.4	2180.2	391.2
	5	54.5	1.1	91.1	10.5	2.3	0.1	14.8	2.3	2458.3	322.7
	10	58.1	1.7	31.5	8.0	2.9	0.2	16.6	3.1	911.9	260.8
	15	64.9	3.5	12.4	2.4	3.5	0.1	18.1	2.5	368.9	93.8
55	0	43.5	5.3	99.1	37.1	1.5	0.2	8.9	1.3	2033.3	951.8
	1	45.3	3.3	114.8	3.9	1.4	0.1	8.9	1.1	2374.6	208.8
	5	52.0	2.4	81.7	18.6	2.0	0.2	10.5	1.5	2063.2	513.6
	10	56.5	1.3	32.6	4.2	2.5	0.2	12.3	2.5	886.7	130.0
	15	61.6	2.6	13.2	1.8	3.0	0.1	16.9	1.7	359.1	63.0

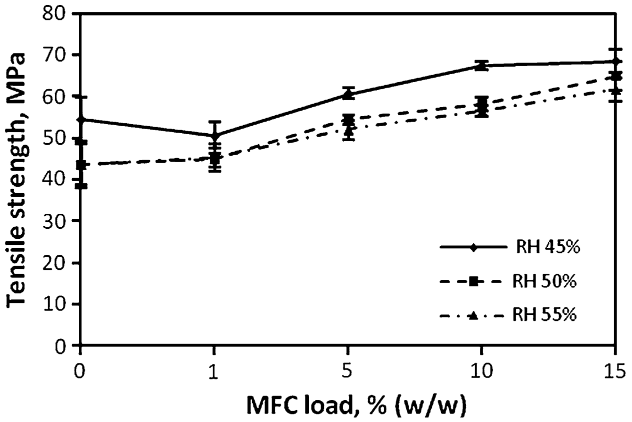

Fig. 11 Comparison of composites tensile strength with respect to different relative humidity

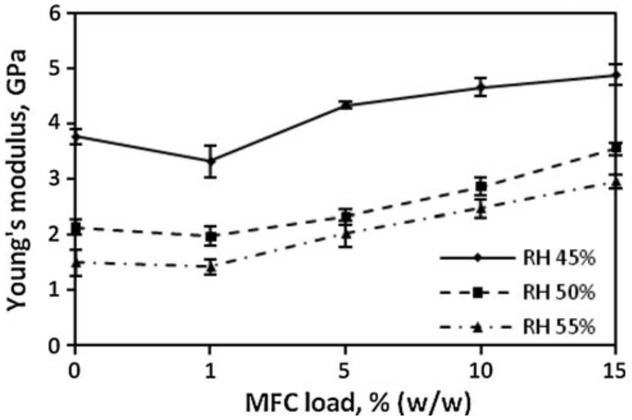

Fig. 12 Comparison of composites Young's modulus with respect to different relative humidity

stiffness are to be considered. The work of fracture is significantly decreased at 10% (w/w), but reaches a plateau at 15% (w/w). The trend is similar to that presented in Table 1, indicating that there is no essential difference in the behaviour of composites within the samples tested in the same environment. The values of work of fracture between the groups are not significantly different; however, there is some indication that it was slightly lower at a RH of 45%. Most probably higher Young's modulus at a lower relative humidity counterbalance the lower strain at break and results is unchanged work of fracture. The mechanical behaviour of composites was different at 45 %RH as the stress–strain curves indicate in Fig. 13. It is known that water molecules plasticise PVA chains. The differences in mechanical properties can be assigned to the change of in the glass transition temperature (T_g). As reported by Roohani et al. [8] T_g decreases as relative humidity increases at constant temperature. However, in their study a broader range of RH was investigated.

The strain at break was significantly smaller at 45 %RH in comparison to 50 and 55 %RH. However, no significant difference was observed between 50 and 55 %RH in terms of strain at break as well as Yield strength. Difference in strain at break increases as the load of microfibrils increases. It is around 10% for pure PVA film and reached a threefold difference at 15% (w/w) MFC load. The behaviour is mainly determined by the matrix, since the trend can be observed in pure PVA specimens. The mechanical behaviour at 50 or 55 %RH is clearly different. This is an indication that the permitted deviation for the standard atmosphere class 1 by the standard ISO 291:2008 has to be carefully considered when performing the test. The results can be very misleading if the relative humidity is not tracked very carefully.

Experimental results comparison to theoretical models

The experimental data observed in this work was compared with theoretical models. The comparison is presented in Fig. 14.

The theoretical modelling based on the modified rule of mixtures and percolation theory is in good agreement with experimental data (B1 composite). There was a slight drop in Young's modulus at lower MFC contents [<5% (w/w)] in the experimental data. The fibre–fibre interactions at low contents of reinforcement agent are limited; therefore, they tend to form clumps which in turn might slightly degrade the mechanical properties. Rule of mixtures and Halpin-Tsai models seems to overestimate reinforcement phenomena. It could be due to the fact that the models assume perfect fibre shape and homogeneous properties in addition to perfect bond between matrix and fibre. The lower empirical values obtained are likely due to imperfections in fibres, moderate dispersion of fibres, fibre-matrix bonding failure and other flaws such as entrapped air. In the case of the Halpin-Tsai model the variation in the aspect ratios makes modelling difficult. In our study aspect ratio was assumed to be 50. In contrast to the rule of mixtures and Halpin-Tsai model, the modified rule of mixtures treats the composite as two macroscopic phase system, i.e. assumes fibre/matrix debonding at the interface. Percolation theory evaluates fibre–fibre interactions. Both of them provide better agreement with experimental data, thus implying that many different factors have to be considered in order to understand reinforcement phenomenon.

Conclusions

Composites with different loads of reinforcement agent were prepared and tested. The results showed that

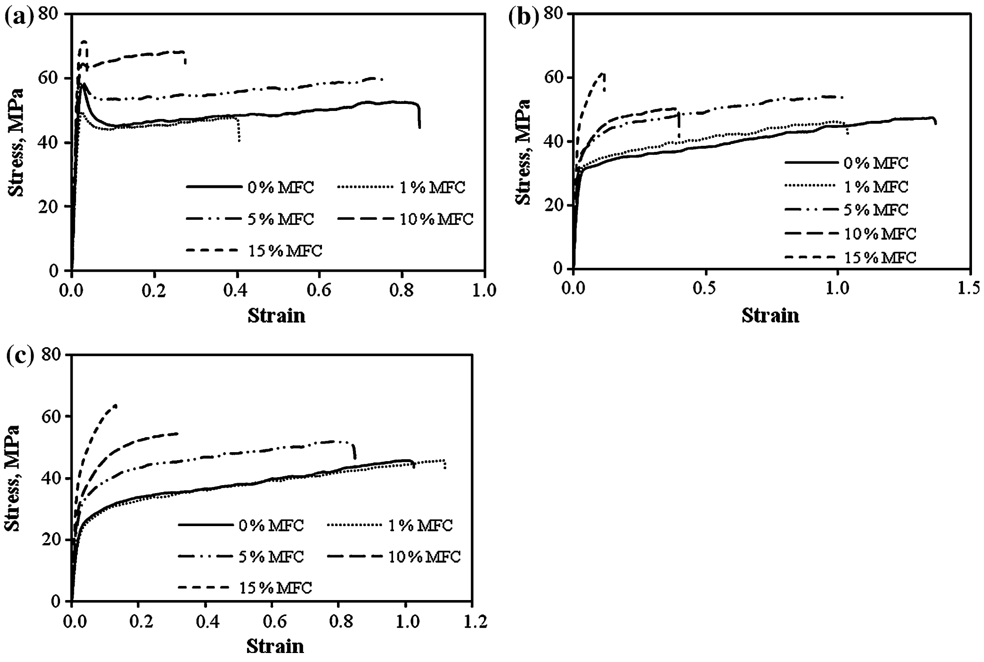

Fig. 13 The mechanical behaviour of composites depending on relative humidity. **a** 45 %RH; **b** 50 %RH; **c** 55 %RH

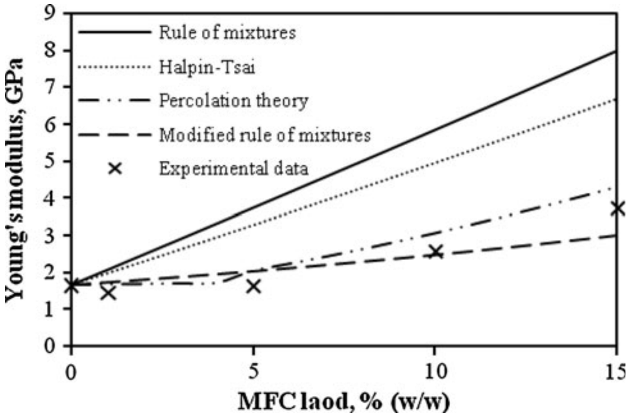

Fig. 14 Comparison of experimental data to models

reinforcement took place at MFC loads over 5% (w/w). Consequently, tensile strength, Young's modulus and yield strength were increased. However the toughness decreased significantly at the MFC loads over 10% (w/w). The concentration of matrix solution had an influence on distribution of fibres and consequently on the mechanical properties. Young's modulus was found to be lower at lower concentrations of polymer below 10% (w/w) MFC load and higher over 10% (w/w) MFC load. Degassing of the dispersion improves mechanical properties below 10% (w/w) load and degrades it when the MFC load increases. The density of pure PVA film was increased by degassing, meanwhile composite density did not changed. The densities of composites were slightly increased by the addition of MFC, but over 5% (w/w) it plateaus. The mixing time was observed to have negative influence on the strength properties of the polymer and consequently on the composite. The results imply that the mechanical properties of composites prepared by different methods are not comparable. In addition, testing at different levels of RH showed that although the standard permitted deviation of ±5% might be maintained the mechanical properties may differ significantly. Therefore, the deviation in RH should be lower to have reliable results.

The experimental data depart from the theoretical models of Halpin-Tsai and rule of mixtures, but shows good agreement with the percolation model and modified rule of mixtures.

Acknowledgements Authors would like to thank the Academy of Finland (decision number 12706) for financial support and DuPont Finland for providing poly(vinyl) alcohol. Thanks to Alexander Perros for help with SEM imaging.

References

1. Lars B (2005) In: Amar MK, Manjusri M, Drzal LT (eds) Natural fibers, biopolymers and biocomposites. Taylor & Francis, Routledge
2. William HBrown (ed) (1988) Introduction to organic chemistry, 4th edn. Brooks/Cole publishing company, California
3. Azizi SM, Said A, Alloin F, Dufresne A (2005) Biomacromolecules 6:612
4. Hubbe MA, Rojas OJ, Lucia LA et al (2008) BioResources 3:929
5. Dufresne A (2008) Can J Chem 86:484
6. Eichhorn SJ, Dufresne A, Aranguren M et al (2010) J Mater Sci 45:1. doi:ESI-2010-007
7. Orts WJ, Shey J, Imam SH et al (2005) J Environ Polym Degr 13:301
8. Roohani M, Habibi Y, Belgacem NM et al (2008) Eur Polym J 44:2489

9. Gopalan NK, Dufresne A (2003) Biomacromolecules 4:657
10. Samir M, Alloin F, Dufresne A (2005) Biomacromolecules 6:612
11. Garcia DR, Thielemans W, Dufresne A (2006) Cellulose 13:261
12. Nakagaito AN, Yano H (2004) Appl Phys A 78:547
13. Zimmermann T, Pöhler E, Geiger T (2004) Adv Eng Mater 6:754
14. Nakagaito AN, Yano H (2005) Appl Phys A 80:155
15. Chakraborty A, Sain M, Kortschot M (2006) Holzforschung 60:53
16. Lu J, Wang T, Drzal LT (2008) Compos A 39:738
17. Cheng Q, Wang S, Rials T et al (2007) Cellulose 14:593
18. Cheng Q, Wang S, Rials TG (2009) Compos A 40:218
19. Tang C, Liu H (2008) Compos A 39:1638
20. Billmeyer FWJ (1984) Textbook of polymer science. Wiley, Singapore
21. Food and Agriculture Organization of the United Nations (FAO) and the World Health Organization (WHO) (2004) Polyvinyl alcohol. ftp://ftp.fao.org/es/esn/jecfa/cta/CTA_61_PVA.pdf. Accessed 27 Nov 2010
22. Li H (2000) Macromolecules 33:465
23. Cinelli P, Lawton JW, Gordon SH et al (2003) Macromoleculars no. 197:115
24. Said AS, Alloin F, Paillet M et al (2004) Macromolecules 37:4313
25. Nakagaito A, Yano H (2008) Cellulose 15:555
26. Lu J, Askeland P, Drzal LT (2008) Polymer 49:1285
27. Sakurada I, Nukushina Y, Ito T (1962) J Polym Sci 57:651
28. Cheng Q, Wang S, Harper DP (2009) Compos A 40:583
29. Cox HL (1952) Br J Appl Phys 3:72
30. Davies WEA (1971) J Phys D 4:1176
31. Davies WEA (1971) J Phys 4:318
32. Hill R (1963) J Mech Phys Solids 11:357
33. Hill R (1964) J Mech Phys Solids 12:213
34. Affdl JCH, Kardos JL (1976) Polym Eng Sci 16:344
35. Allen G, Bowden MJ, Todd SM et al (1974) Polymer 15:28
36. Favier V, Chanzy H, Cavaille JY (1995) Macromolecules 28:6365
37. Favier V, Cavaille JY, Canova GR et al (1997) Polym Eng Sci 37:1732
38. Chazeau L, Cavaillé JY, Canova G et al (1999) J Appl Polym Sci 71:1797
39. Ouali N, Cavaille JY, Perez J (1991) Plast Rubber Compos Process Appl 16:55
40. Aharony A, Stauffer D (1994) Introduction to percolation theory, 2nd edn. Taylor & Francis, UK
41. Young RJ, Lovell PA (1991) Introduction to polymers, 2nd edn. Chapman & Hall, Cambridge
42. Taghizadeh MT, Mehrdad A (2003) Ultrason Sonochem 10:309
43. Alexy P, Lacík I, Šimková B et al (2004) Polym Degrad Stab 85:823