



Barrier and sorption properties of porous poly(vinyl alcohol)–cellulose fibre composites

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Abstract. Various composites were prepared by impregnation of cellulose fibre nonwovens (CFNs) with poly(vinyl alcohol) using two methods. The composites obtained contained up to 0.4 volume fraction of polymer, and the volume fraction of voids was not less than 0.3. Scanning electron microscope images show no great changes in CFN frame structure compared to untreated CFN. Air and water vapour permeability decreases with growth of the volume fraction of polymer as a result of filling of the voids and formation of closed voids. As determined by sorption characteristics, the composite and its base absorb water vapour differently from CFNs. Biodegradation of samples in soil was inspected. Test data show a faster degradation for samples with a small polymer amount, where less than 10% of initial weight is left after two weeks exposure in soil.

Key words: material science, cellulose fibre nonwovens, poly(vinyl alcohol), structure, barrier properties, biodegradability.

INTRODUCTION

Large amounts of plastics are used to package various products. Since packaging is a short-term product, its proportion in waste dumps is remarkable. At the same time public concern over dwindling landfill space and accumulation of surface litter increases. Biodegradable materials can notably contribute to reducing the growing waste problem caused by different petrochemical materials [1].

Cellulose-based materials are one of the main raw materials used in packaging. They are widespread, renewable, and with great strength at a relatively low cost [2,3]. Cellulose fibre nonwovens (CFNs) as natural polymers are environmentally friendly and biodegradable materials.

Poly(vinyl alcohol) (PVA) is a widely produced water soluble and completely biodegradable synthetic polymer. It is easy to process and has good mechanical characteristics. Thus PVA is an excellent constituent for green composites. Degradation of PVA is quite slow and largely depends upon such structural properties as the degree of polymerization and hydrolysis, distribution of

hydroxyl groups, stereoregularity and crystallinity [4]. However, composites with cellulose materials can accelerate the process of degradation [2,5] and offer new industrial applications in many fields [6].

Many packaging applications demand certain barrier properties as well as mechanical resistance. It is generally recognized that loss or gain of moisture plays a critical role in assessing the quality and shelf life of packaged food. Due to their hydrophilic nature, cellulose fibres tend to absorb water vapour from the environment, especially, under high-humidity conditions, as well as grease and oil. In addition, resistance to grease is also a property which should be improved, and biopolymers can provide it. Moisture sorption induces alterations in mechanical properties of CFNs, which has led to the need for combining cellulose packaging materials with polymers. Cellulose fibre nonwovens are a perspective base for targeted further treatment to create a packaging with a better barrier or other functional properties [3,7,8].

Barrier properties of plastic packaging play a great role in designing suitable materials. The vapour transmission rate has significance in considering the selection of barrier materials for hygroscopic foods. The gas transmission rate helps in material selection for, e.g., oxygen-

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sensitive foods, and for some products resistance to grease is important [1].

The main objective of this work was to study the barrier and biodegradation characteristics of CFN–PVA composites and to assess correlation of these characteristics with their microstructural features. Mechanical properties of these composites were investigated in [9–11] in particular. The development of nature-friendly biodegradable packaging materials is a topical problem. Conjunction of such widespread materials as cellulose and PVA can be both practical and economically advantageous.

MATERIALS AND METHODS

On the basis of previous studies [12] three dissimilar CFNs with different voids content (Table 1) were chosen for impregnation with PVA water solutions. Partly crystalline water-soluble PVA was used (molecular weight 133 kDa, density 1.28 g/cm³, content of acetate groups 0.98 wt%) and PVA solutions with various polymer concentrations (7–15%) were prepared.

The composites were prepared by two different methods: the applicator method (AM) and the calender method (CM). In accordance with the AM, polymer solution was laid on the nonwoven by casting and subsequent drawing of the applicator along the sample. In case of the CM, the impregnated sample was squeezed once between elastomer-coated calender rolls.

The amount of polymer in the composite was controlled by use of solutions with different polymer contents as well as by applying different gap heights to both the applicator and calender rolls. The prepared samples were stored at 17°C till complete drying.

The following designations were used for characterization of structural parameters: φ – volume fraction; V – volume, cm³; m – weight, g; ρ – density, g/cm³; POL – polymer; C – composite, M – CFN.

The volume fraction of voids in a CFN, φ_{VM} , was estimated as follows:

$$\varphi_{VM} = V_{VM}/V_M, \quad (1)$$

where V_{VM} – volume of voids in the composite, $V_{VM} = V_M - V_{CELM}$; V_M – volume of the CFN sample, $V_M = h_M S$; h_M – thickness of the CFN sample, S – area of the sample (100 cm²); V_{CELM} – volume of cellulose fibres in the

CFN, $V_{CELM} = m_M/\rho_{CEL}$; m_M – weight of the CFN sample; ρ_{CEL} – density of cellulose (1.52 g/cm³).

The amount of polymer in the obtained composites was calculated by the formula

$$\varphi_{POLC} = V_{POLC}/V_C, \quad (2)$$

where φ_{POLC} – volume fraction of polymer in the composite; V_{POLC} – volume of polymer in the composite, $V_{POLC} = m_{POLC}/\rho_{POL}$; m_{POLC} – polymer weight in the sample, ρ_{POL} – density of polymer; V_C – volume of the composite sample, $V_C = h_C S$; h_C – thickness of the composite sample.

The volume fraction of cellulose fibres in the composite, φ_{CELC} , was evaluated as follows:

$$\varphi_{CELC} = V_{CELM}/V_C, \quad (3)$$

where V_{CELM} – volume of cellulose in the CFN.

The volume fraction of voids in the composite, φ_{VC} , was determined as follows:

$$\varphi_{VC} = V_{VC}/V_C, \quad (4)$$

where V_{VC} – volume of voids in the composite sample, $V_{VC} = V_C - (V_{POL} + V_{CELM})$.

The structure of a CFN and its composite were studied on the Tescan, Mira/LMU Shottky scanning electron microscope (SEM) at the $\times 600$ magnification and voltage of 15 kV. Samples for tests were cooled in liquid nitrogen and fractured by bending. Brittle fracture cross sections were covered with gold (Emitech, K550X) [2].

Air permeability q was estimated as a mean value of five parallel results according to the standard EN ISO 9237 [13] by measuring the air flow (L/min) through a 5 cm² area under 2 kPa pressure differences on the air permeability device “SDL Atlas”.

Water vapour transmission (WVT) was evaluated by the desiccant method according to the standard ASTM E 96 [14]. Test specimens were sealed to a test dish containing anhydrous calcium chloride (desiccant). The sets were stored for four weeks in relative humidity 50 ± 2% at 32°C and periodically weighed. Water vapour transmission (g/h × m²) was calculated as follows:

$$WVT = (G/t)/A, \quad (5)$$

where G – weight change, g; t – time during which G occurred, h; A – test area (dish mouth), m².

Table 1. Characterization of cellulose fibre nonwovens (CFN)

CFN	Thickness h , μm	Density ρ , g/cm ³	Volume fraction of voids, φ_V	Average fibre length l , mm	Tensile strength σ_B^{\parallel} , MPa	Tensile strength σ_B^{\perp} , MPa	$\sigma_B^{\parallel}/\sigma_B^{\perp}$
CFN I	156	0.46	0.70	2.0	17.7	8.0	2.2
CFN II	136	0.67	0.56	0.9	53.9	21.1	2.6
CFN III	162	0.91	0.40	0.8	53.51	22.7	2.4

Hygroscopic properties of composites were determined following the requirements of the standard ASTM D 3201 [15]. Samples were exposed in 97% relative humidity (maintained by 3% calcium chloride solvent) at a temperature of 25°C for seven days and dried in an oven at 105°C until constant weight was attained. “Apparent” moisture content w (%) prior (6) and after (7) high-humidity exposure was calculated to find out the ratio w_A/w_P using the formulas

$$w_P = ((m - m_D)/m_D) \times 100, \quad (6)$$

$$w_A = ((m_W - m_D)/m_D) \times 100, \quad (7)$$

where w_P – moisture content prior to high-humidity exposure, w_A – moisture content after high-humidity exposure, m – sample weight prior to high-humidity exposure, m_D oven-dry sample weight, m_W – sample weight after high-humidity exposure.

Biodegradation of CFNs and their composites was determined by the soil burial test. A sample of 3 × 3 cm size was inserted in the Petri dish with humidified soil to imitate conditions in the environment and exposed to 25°C temperature. After the defined time periods samples were removed from soil, cleansed, and weighed.

$$z = (m_0 - m_E)/m_0 \cdot 100\%, \quad (8)$$

where z – weight loss, %; m_0 – initial sample weight, g; m_E – sample weight after exposing in soil, g.

RESULTS AND DISCUSSION

The main components building a CFN are cellulose fibres and voids. The length and width distribution of cellulose fibres was discussed in [10]. Schematic depiction of composite structure is shown in Fig. 1. The CFN samples contain a small amount of adhesives and fillers. Composites with the volume fraction of polymer up to 0.4 and the volume fraction of voids up to 0.3 were prepared.

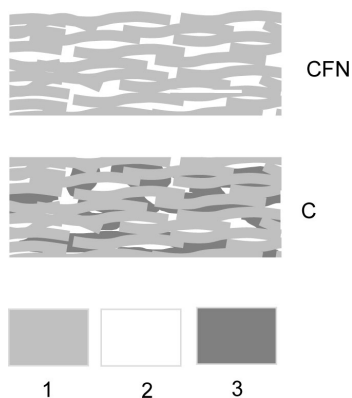


Fig. 1. Scheme of the CFN and composite structure (1 – cellulose fibres, 2 – voids, 3 – polymer).

The SEM images of the composite do not reveal significant changes in CFN structure in comparison with untreated CFN. Although slight compacting of CFN structure and a thin polymer layer around and among the fibres for all composites can be observed, no remarkable alteration of CFN structure occurred (Fig. 2) [10].

The ternary phase diagram (Fig. 3) shows the relationship between the contents of all three components of the composite, i.e., volume fractions of cellulose, voids, and polymer. To ensure certain permeability of gas and/or moisture, which is essential for potential use of composite as packaging material, our aim was not to reach the volume fraction of voids less than 0.3. Therefore the values of the components contents on the diagram are rather closely spaced. The more porous CFN, the more polymer solution it can accumulate. The volume fraction ϕ_{POL} up to 0.4 in composites can be reached on the basis of the most porous CFN I. The diagram proves that the AM technique allows greater impregnation of nonwovens than the CM technique.

As expected, the air permeability q of composites declines considerably with increase in polymer content (Fig. 4a). Values of air permeability q drop about 2–3 times for composites with a small polymer content ($\phi_{POL} < 0.10$), in comparison with untreated CFN (Fig. 4b). The q values decrease by about one order for composites made by the CM technique and even more than 50 times for CFN I samples with a high polymer content ($\phi_{POL} \sim 0.4$) prepared by the AM technique.

A general trend can be noted: while the volume fraction of voids in the composite reduces almost linearly (as a consequence of structural permanence of CFN [10]), air permeability drops sharply (Fig. 5). Even small amounts of polymer cause multiple decay of permeability, most probably due to the formation of closed voids.

Another important characteristic of packaging materials, WVT, was evaluated for the period of four weeks. Figure 6 represents the principle of the WVT process, i.e., steady mass increase in test sets which indicates continuous permeability. The WVT values are specified in Table 2. Since the WVT of PVA is comparatively low – 0.15 g/(h m²), the WVT values of composites are considerably lower relating to base material. The higher ϕ_{POL} value, the lower is transmission ability (Fig. 7).

The amount of absorbed water vapour at the equilibrium state of untreated CFN is in the range 12–18%. Figure 8 indicates the change in the moisture content of the same sample after and before the experiment. Quite a great amount of moisture has absorbed all composites. Composites CFN I and CFN II absorbed less moisture than an untreated nonwoven, while composite CFN III absorbed more. It seems that CFN I and CFN II are more hydrophilic than polymer, and treatment with polymer makes water vapour sorption

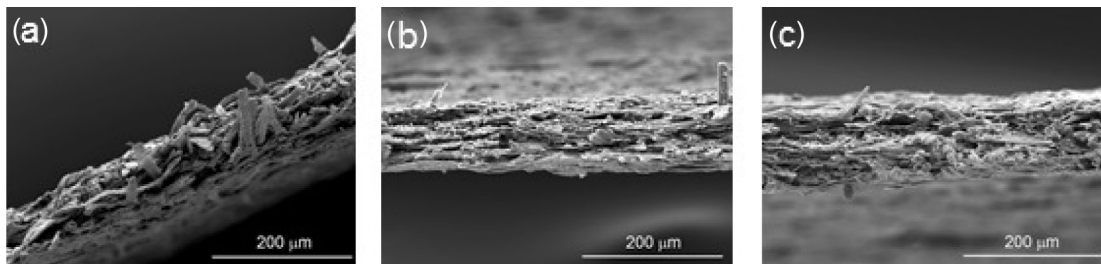


Fig. 2. SEM images of CFN II: untreated (a) and impregnated ($\phi_{POL} = 0.02$ (b); $\phi_{POL} = 0.06$ (c)).

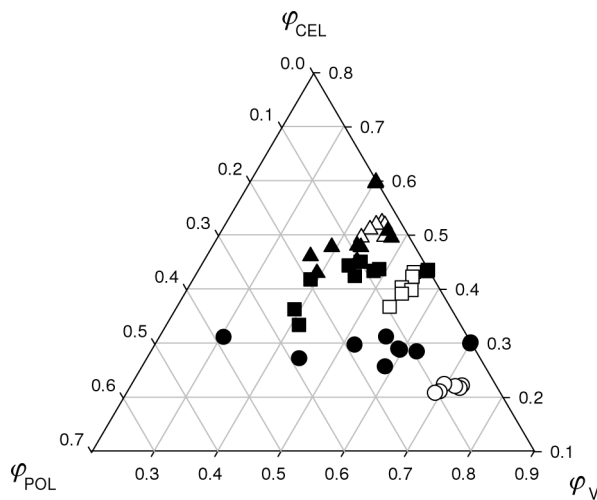


Fig. 3. Ternary phase diagram (\circ – CFN I (AM), \bullet – CFN I (CM), \blacksquare – CFN II (AM), \square – CFN II (CM), \triangle – CFN III (AM), \blacktriangle – CFN III (CM)).

more limited, whereas CFN III appears more hydrophobic and PVA accelerates water vapour absorption.

Biodegradation tests confirm that composites with a small polymer content ϕ_{POL} lose their integrity and weight more rapidly than those containing more polymer, even faster than untreated CFNs (Fig. 9). Already after two weeks of experiment less than 10% of sample initial mass was left for all three untreated non-wovens with $\phi_{POL} \leq 0.6$ and no more than 40% for base material and composites with a higher ϕ_{POL} . Composites with little ϕ_{POL} were completely degraded when four weeks had passed, whereas base material and composites with higher ϕ_{POL} had lost at least 80% of their initial mass. It should be noted that further degradation occurs slowly, particularly disintegration of composites. However, after six weeks no CFN I and CFN III samples were left in the test dish. The results derived show that changes in structure after incorporation of polymer are of great importance for microorganisms consuming it.

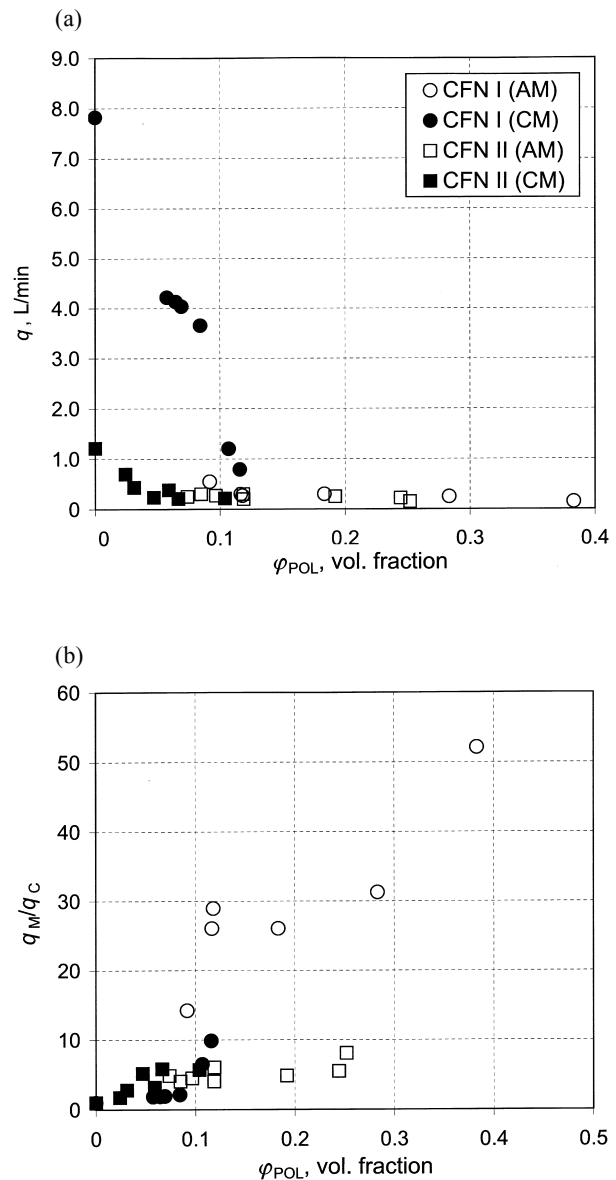


Fig. 4. Air permeability values q_C (a) and ratio q_M/q_C (b) of composites as function of polymer content.

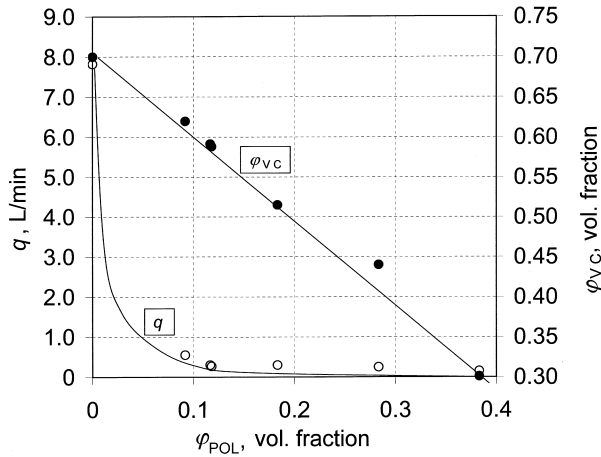


Fig. 5. Air permeability q and volume fraction of voids φ_{VC} versus volume fraction of polymer φ_{POL} in the composite.

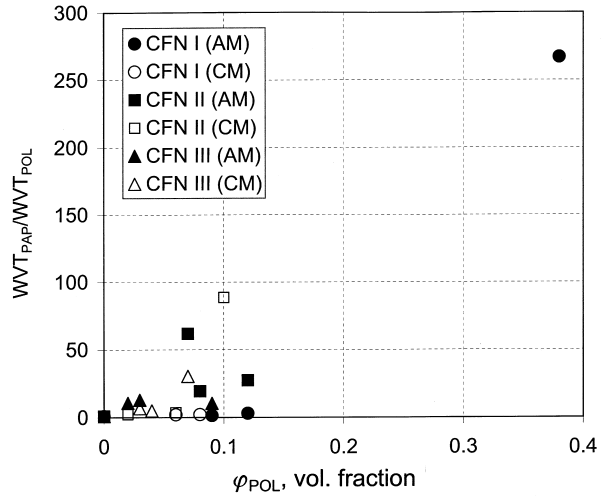


Fig. 7. Relative water vapour transmission of composites.

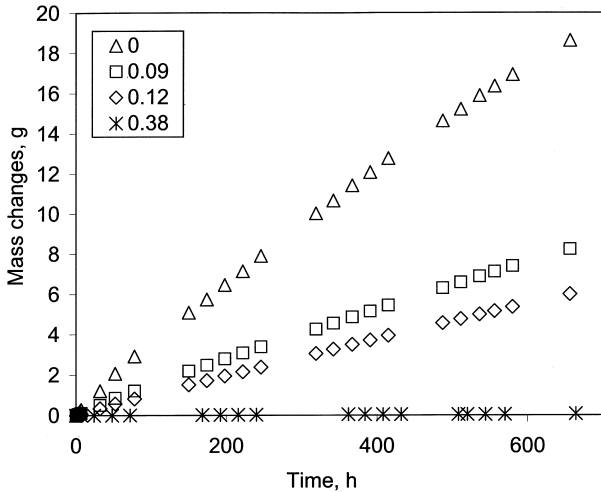


Fig. 6. Dynamics of mass increase during the water vapour transmission test for CFN I composites (figures at the symbols – volume fraction of polymer).

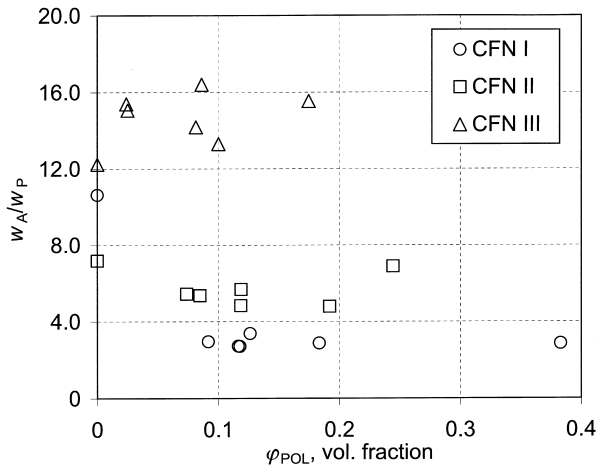


Fig. 8. Comparison of sample moisture content after (w_A) and prior to (w_P) water vapour sorption by the applicator method.

Table 2. Water vapour transmission (WVT) values, $g/(h\ m^2)$, for cellulose fibre nonwovens (CFN) and composites determined by the applicator (AM) and calender (CM) methods. φ_{POL} – polymer content

Method	CFN I		CFN II		CFN III	
	φ_{POL}	WVT	φ_{POL}	WVT	φ_{POL}	WVT
AM	0	18.67	0	19.41	0	13.11
	0.09	8.26	0.07	0.31	0.02	1.28
	0.12	6.02	0.08	0.69	0.03	1.47
	0.38	0.07	0.12	0.43	0.09	1.22
CM	0.06	9.13	0.02	8.45	0.03	2.11
	0.08	8.41	0.06	5.52	0.04	2.41
	0.12	3.28	0.10	0.22	0.07	0.43

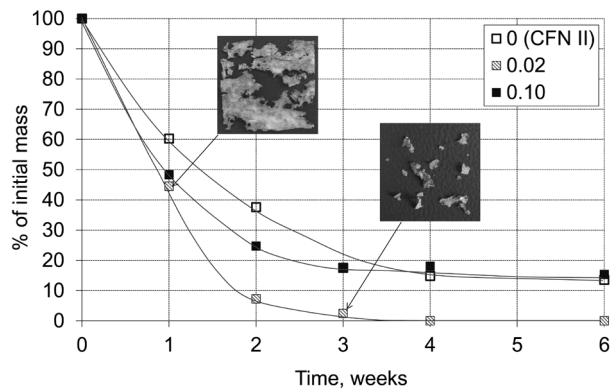


Fig. 9. Course of biodegradation of CFN II and its composites with different polymer contents studied by the calender method (figures at the symbols – volume fraction of polymer).

CONCLUSIONS

Composites based on CFNs with different volume fraction of voids φ_{VM} (0.70, 0.56, and 0.40) and poly(vinyl alcohol) were made. Volume fraction of polymer, φ_{POL} , for obtained materials is within the range 0.02–0.38 and volume fraction of voids in composite, φ_{VC} , is from 0.30 to 0.70. The polymer amount was controlled by using different concentrations of polymer solution, two methods of sample preparation, and various gap heights of apparatus.

SEM microphotos disclose no great changes in CFN frame structure compared to untreated CFNs.

As predicted, air and water vapour transmission declines with increase in the volume fraction of polymer, most probably due to filling of voids with polymer and formation of closed voids.

The water vapour sorption character observed suggests that absorption is determined by the hydrophobic/hydrophilic nature of CFNs.

Fast biodegradation of composites takes place in the first two weeks when more than 90% of the initial weight of composite with $\varphi_{POL} \leq 0.06$ disintegrates. After this period degradation continues much slower, except CFNs with a small polymer amount that disintegrate completely. This indicates that the process of degradation depends on the availability of both cellulose and polymer.

The tests performed show that barrier and sorption properties as well as biodegradability of the obtained composites meet the packaging requirements.

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Poorse polü(vinüülalkohol)tselluloosi kiudkomposiitide barjääri- ja sorptsiooniomadused

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Tsellulooskiust mittekootud materjalide (CFN) immutamisel polüvinüülalkoholiga valmistati mitmesuguseid komposiite kahel meetodil. Saadud komposiidid sisaldasid kuni 0,4 mahuprotsenti polümeeri ja tühimike osakaal oli vähemalt 0,3 mahuprotsenti. Töötlemata CFN-idega võrreldes ei ole SEM-kujutistel märkimisväärseid struktuuri muutusi näha. Tühimike täitumisel ja sulgumisel vähenevad polümeeri mahuosa suurenedes õhu ning veeauru läbilaskvus. Sorptsioonikarakteristikutest nähtub, et komposiidid absorbeerivad veeauru CFN-idest erinevalt. Biolagunemise katsed mullas näitavad, et kiiremini lagunevad vähese polümeerisisaldusega proovid: kahepäevase ekspositsiooniperioodi järel on algsest kaalust alles vähem kui 10%.