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PRODUCTION AND PROPERTIES OF BIOPOLYMER COMPOSITES USING NATURAL CELLULOSE FIBRES AS REINFORCEMENT

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Annotation

This research work is focused on study of problems, characterisation and possibilities of composite systems utilisation with filler from hydrophilic natural cellulose fibres (bamboo, flax, hemp and recycled paper – PSP) embedded into the various polymer matrices (hydrophobic thermoset epoxy resin – EP and thermoplastic polypropylene – PP, and hydrophilic thermoplastic polyvinyl alcohol – PVA). Adhesion between fibres and polymer matrices was studied. Two ways of modification were followed – utilisation of maleic anhydride – MAPP coupling agent and surface treatment of polymer particles by cold plasma.

The thesis is subdivided into theoretical and into experimental part. The second one has three main parts:

1. measurement of mechanical properties – tensile strength and Young's modulus of used polymers and produced composite systems with filler from cellulose fibres in dependence on filling fraction;
2. defibrillation of natural cellulose fibres;
3. measurement of water absorption of complete composite systems and cellulose fibres.

Evaluation of tensile strength and Young's modulus in dependence on fibres type and their amount were measured on the basis of tensile test. Homogeneity of prepared test pieces and adhesion between fibres and polymer matrix were checked by SEM. The water absorption of prepared composite systems and the cellulose fibres was characterised by measuring its initial and final mass.

Dependence of mechanical properties on filling fraction was proved according to theory in majority cases. The highest increase (by 50 %) of tensile strength was found for PP filled with 4 wt. % of MAPP and 30 wt. % of PSP fibres and for moulded PVA with the same amount of PSP fibres. The best results of Young's modulus (increase by 600 %) were obtain after embedding 30 wt. % of hemp fibres to the cast PVA matrix.

Defibrillation technology of natural cellulose fibres was developed. Improvement of aspect ratio and overall adhesion of cellulose fibres to polymer matrix was proved.

Study of the water absorption proved an enhancement of resulting composites after incorporation of natural cellulose fibres to the polymer matrices. Embedded 9 wt. % of PSP fibres maximally enhanced the water absorption by 2 500 %, in case of EP matrix.

Homogenisation that was influenced by processing method significantly impacted properties of the composite systems. Extrusion followed by injection moulding was superior to cast method.

Key words: *natural cellulose fibres; fibre – polymer matrix adhesion; mechanical properties of composites; defibrillation; water absorption.*

Anotace

Tato práce se zabývá problematikou využití přírodních rostlinných vláken (bambusu, lnu a konopí) a celulózových vláken z recyklovaného papíru (PSP) jako vyztužujících prvků syntetických polymerních matric na bázi reaktoplastů (EP) a termoplastů (PP, PVA) a výběrem vhodné metody pro přípravu vzorků.

Zásadní odlišnost v hydrofilitě použitých složek (kromě PVA), vedla ke studiu možností zkvalitnění adheze mezi použitými matricemi a vlákny. K ovlivnění charakteru mezifázového rozhraní bylo využito chemické cesty, úpravy polymerní matrice vazným činidlem (anhydridem kyseliny maleinové MA) a způsobu fyzikálního, při kterém byl povrch částic polymeru určeného k dalšímu zpracování upraven studeným plazmatem.

Práce je rozdělena na část teoretickou, předkládající současný stav problematiky a část experimentální, ve které jsou na základě zkoušky tahem hodnoceny základní mechanické parametry (mez pevnosti v tahu a Youngův modul pružnosti) vyrobených vzorků v závislosti na množství použitých vláken ve zvolené polymerní matrici. Z charakterů lomových ploch sledovaných vzorků posuzovaných rastrovací elektronovou mikroskopií byla hodnocena homogenita kompozitních systémů a kvalita dosaženého mezifázového rozhraní. Dále pak na základě mikroskopického stanovení rozměrů celulózových makrofibril a mikrofibril byl sledován stupeň defibrilace celulózových PSP vláken a měřením navlhavosti samotných celulózových vláken i vzorků kompozitních materiálů byla doplněna představa o hydrofilitě vznikajících systémů.

Z hodnocení provedených experimentů je zřejmé, že plniva na bázi celulózových vláken přispívají pozitivně ke změně základních mechanických parametrů. K nejvýraznějšímu zvýšení meze pevnosti v tahu (až o 50 %) dochází v případě vstřikovaných vzorků PP modifikovaného anhydridem kyseliny maleinové s 30 hmotnostními procenty PSP vláken stejně jako vzorků PVA s 30 hm. % PSP vláken. Maximálního zvýšení Youngova modulu (až o 600 %) bylo dosaženo v případě odlévaných vzorků PVA s 30 hm. % konopných vláken.

Na základě současných znalostí o metodách defibrilace celulózových vláken byl navržen nový způsob, kterým bylo získáno za použití 10% roztoku NaOH, ultrazvuku a homogenizéru v reálném čase dostatečné množství vodní suspenze celulózových makrofibril a mikrofibril.

Nejvyšší navlhavost (zvýšení až o 2 500 %) byla naměřena u vzorků epoxidové pryskyřice plněné 9 hmotnostními procenty celulózových PSP vláken z recyklovaného papíru.

Z výsledků měření vyplývá, že mechanické vlastnosti připravených kompozitů jsou závislé nejen na typech použitých polymerních matric, na parametrech vyztužujících vláken a kvalitě vytvořeného mezifázového rozhraní, ale i na vzájemné homogenizaci složek systému během zpracování a zvolené metodě zpracování vůbec. Metodu extruze s následným vstřikováním do forem lze pro přípravu vzorků považovat za vhodnější než metodu odlévání z vodných roztoků.

Klíčová slova: *přírodní rostlinná vlákna; adheze vlákno – polymerní matrice; mechanické vlastnosti kompozitů; defibrilace; navlhavost.*

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1 Introduction

Cellulose is a ubiquitous structural polymer that confers its mechanical properties to higher plant cells. A cell wall is a dynamic structure in all terrestrial and aquatic plants. Its constituting material must be synthesised in a form that is able to undergo extension. The primary cell wall is essentially a composite system consisting of a framework of cellulose fibrils embedded in a cementing matrix of other polymers, mostly lignin and hemicelluloses. Cellulose chains are aligned parallel in one axis in order to create elementary fibrils – "nanofibres". This perfect organisation confers to the microfibrils mechanical properties that are close to the theoretical limit of cellulose.

Such microfibrils can be extracted from the biomass by a mechanical treatment followed by a chemical treatment extracting purified cellulose. A mechanical treatment allowed to obtain homogeneous suspensions of aqueous suspensions of individualised microfibrils.

Cellulose fibres – a rediscovered raw reinforcing material – could be used in a number of applications ranging from fibres for plastic, reinforcement to gel forming and thickening agent. These have been reported in a number of papers and patents. Methods have been developed to extract microfibrils not only from wood pulp fibres [1–6] but also from parenchymal cell walls that constitute major leftovers from the food industry [7–16].

Nowadays plant fibres are being accepted as glass fibre replacements in composite manufacturing. Currently cut long vegetable fibres from plants like abaca, bamboo, flax, hemp, jute, sisal or fibres from recycled paper are used. Long fibres are used in form of woven and non-woven textiles. Most of this research has concentrated on using common plant fibres or secondarily thickened, highly elongated fibre cells. These are tens of microns in diameter and may be many millimetres long. However, all plant cells, including those that are not elongated, have the potential to provide reinforcement because each cell can supply cellulose microfibrils with interesting mechanical parameters.

Natural fibres offer several advantages compared with other commonly used artificial fibres (especially glass-fibres):

- Plant Plant fibres are renewable raw material.
- Environmentally friendly qualities, easier health and safety management, potentially lower cost.
- These fibres have a low density, high specific strength and Young's modulus (desirable fibre aspect ratio), and a relatively reactive surface, which can be used for grafting specific groups.
- Cheap waste sources of cellulose material could be used as the starting material for composites manufacture.

- The abrasive nature of these fibres is much lower compared with glass-fibres, which may represent important advantages regarding their processing behaviour, material recycling or process of composite materials in general.
- Natural fibre reinforced plastics by using biodegradable polymers as matrices are most environmentally friendly materials which can be composted at the end of their life cycle.
- At the end of life cycle, plant fibres could be degraded in soil or combusted. The release amount of CO_2 is acceptable for the environment. Leftovers of fibres could be used as fertilisers, too.

Cellulose fibres in connection with biodegradable polymers offer use of composites as fully biodegradable materials. Biodegradable polymers are a re-emergent field. A vast number of biodegradable polymers have been synthesised and some microorganisms and enzymes capable of degrading them have been identified.

Environmental pollution by synthetic polymers has assumed dangerous proportions in developing countries. As a result, attempts have been made to solve these problems through slight modifications of polymers structures and make these everyday use polymers biodegradable.

The thesis is subdivided into a theoretical and to an experimental part. Results of the experiment have three main parts: defibrillation of natural cellulose fibres, measurement of water absorption of fibres and complete composite systems and mechanical properties – tensile strength, Young's modulus, strain of used polymers (hydrophilic thermoplastic polyvinyl alcohol, hydrophobic thermoplastic polypropylene and hydrophobic thermoset epoxy resin) and produced composite systems with hydrophilic cellulose fibres (bamboo, flax, hemp and recycled paper) as filler.

2 Current State of the Art

2.1 Natural Fibres as a Filler

A largely underutilised source of polymeric materials is woody and vegetable biomass. Trees and plants contain cellulose, hemicellulose and lignin, representing an abundant source of renewable polymers that possess high degradability. Cellulose in particular represents the most common existing natural polymer.

A natural plant fibre for example stalk consists of several cells. These cells are formed of crystalline microfibrils based on cellulose as a chain, which is the essential component of all plant fibres. In 1838, Anselme Payen suggested that the cell wall of large numbers of plants consist of the same substance, to which he gave the name cellulose.

It is generally accepted that cellulose is a linear condensation polymer consisting of D-anhydroglucopyranose units (often abbreviated as anhydroglucose units or even as glucose units) jointed together by β-1,4-glycosidic bonds (Fig. 2.1.1.). It is thus a 1,4-β-D-glucan. The pyranose rings are in the $^4C_1$ conformation, which means that the -CH_2OH and -OH groups, as well as the glycosidic bond, are in difference to the starch molecules amylose and amylopectine equatorial with respect to the mean of the rings.

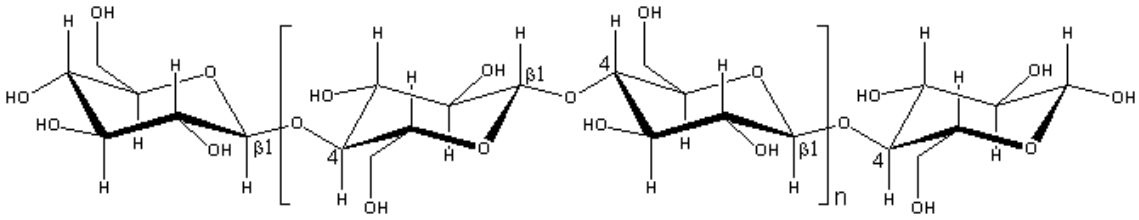


Fig. 2.1.1. Structural unit of cellulose [17].

The molecular structure of cellulose is responsible for its supramolecular structure (Fig. 2.1.2.) and this supramolecular structure determines many of its chemical and physical properties. In the fully extended molecule, adjacent chain units are oriented by their mean planes at an angle of 180º to each other. Thus, the repeating unit in cellulose is the anhydrocellulobiose unit and the number of repeating units per molecule is half the degree of polymerisation. This may be as high as 14 000 in native cellulose, but purification procedures usually reduce it to some value of about 2 500 [6, 12, 17].

The degree of polymerisation shows, that the length of the polymer chains varies depending on the type of natural fibre (Tab. 2.1.1).

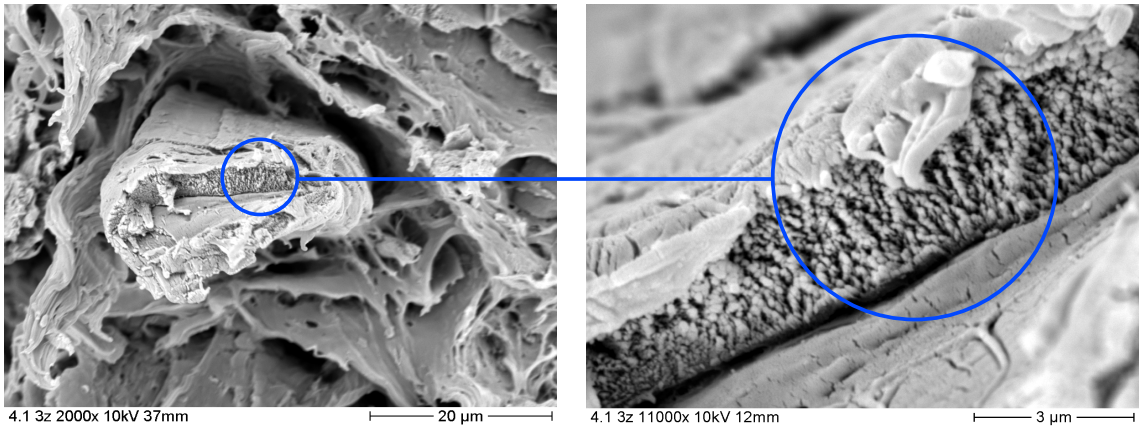
Solid cellulose forms a microcrystalline structure with regions of high order – crystalline regions, and regions of low order – amorphous regions. In native cellulose, one dis-

tinguishes two types of crystal structure, namely I_α and I_β where the cellulose chains are nearly packed in the same way, but in different overall symmetry. Within a given micro-fibril, the cellulose molecules are organised in a perfect parallel mode without any chain folding. Thus, each microfibril can be considered a polymer whisker having mechanical properties approaching those of the theoretical properties of crystal [12]. Naturally oc-curring cellulose (cellulose I_β) crystallises in monoclinic sphenodic structures. The mo-lecular chains are oriented in fibre direction [6, 18–20].

Tab. 2.1.1
Degrees of polymerisation (P_n) of various natural fibres [18]

Fibre	P_n
Cotton	7 000
Flax	8 000
Ramie	6 500

Enzyme rosettes have been found arrayed hexagonally in bundles of 100 or more which wander around the cell membrane leaving behind them a trail of cellulose nanofibre, the so-called elementary fibril approximately 6 nm in diameter containing approximately 40 molecular chains. These aggregate into larger microfibrils in diameter of 5–50 nm and thousands of nanometres long. Figure 2.1.2. shows a micrograph of a fracture surface area of a plant cell wall built up from bundles of these microfibrils. There are many ways of nomenclatures of cellulose fibres and figure 2.1.3. shows one possibility of these ways of sorting. The microfibril is not totally crystalline since it contains sugars other than glucose (usually mannose and xylose) [9, 20]. These microfibrils are connected to a complete layer by amorphous lignin and hemicellulose and withstand normal turgor pressures in the cell and provide the tissue stiffness needed for the plant to function. Theoretical and experimental research has shown that these cellulose microfibrils could have a Young's modulus of up to 130 GPa and strength of up to 7 GPa [10]. Multiple of such cellulose-lignin/hemicellulose layers in one primary and commonly



three secondary cell walls stick together to multiple-layer-composites – the cell wall.

Fig. 2.1.2 Example of real natural composite system – plant cell wall and demonstration of inside structure built up from bundles of macrofibrils – microfibres embedded mainly in secondary cell wall. (Fracture surface of one plant cell embedded in polypropylene matrix.)

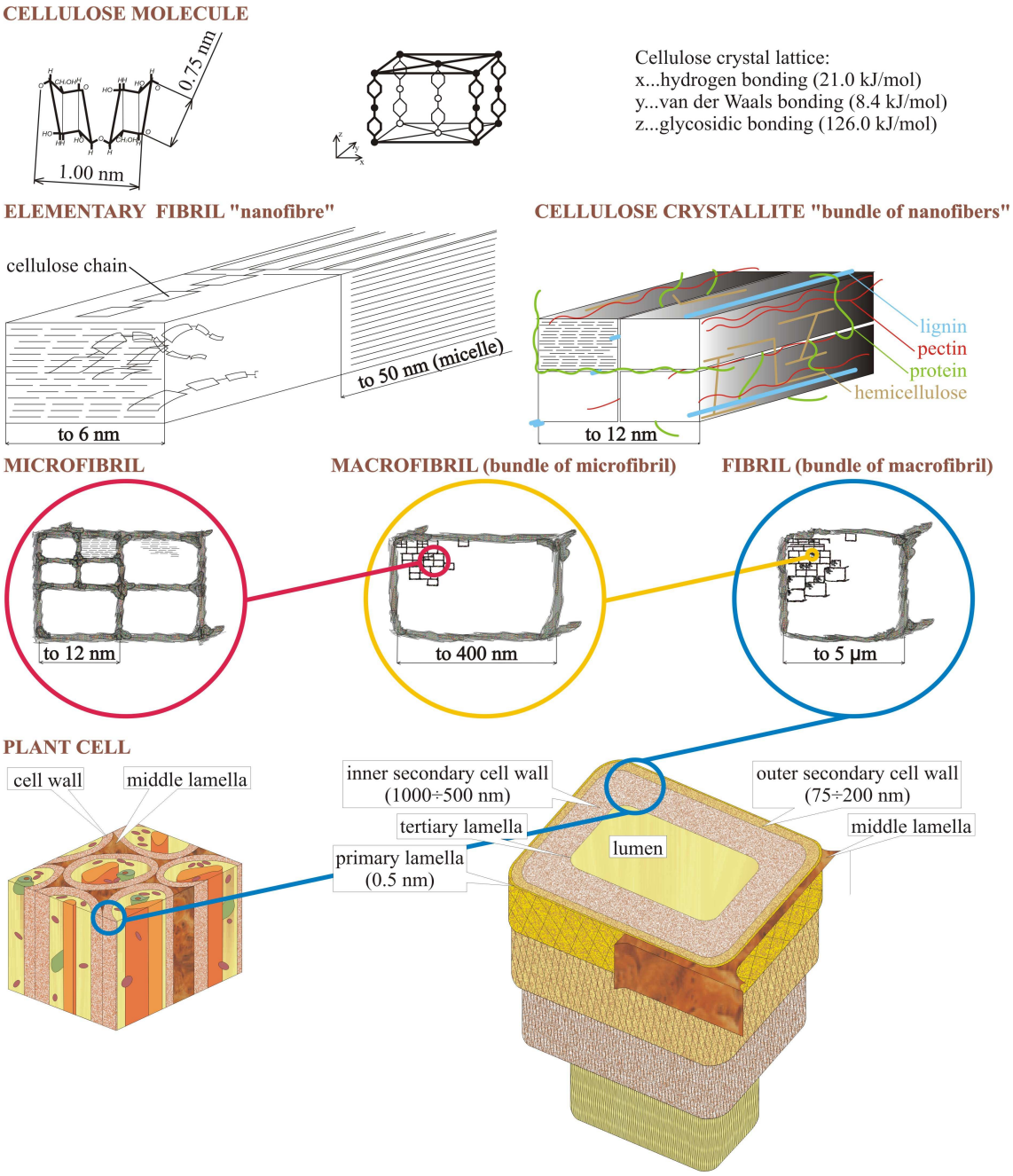


Fig. 2.1.3. Scheme of plant cell architecture. These schematic figures illustrate plant cell architecture from cellulose chains, cellulose micrifibrils and macrofibrils. This scheme was create for important idea of used filler size. Compilation of data from refs. [5, 6, 9, 10, 13–17, 19, 20].

These cell walls differ especially in their composition (the ratio between cellulose, lignin and hemicellulose), in the orientation (spiral angle) of the cellulose microfibrils and in their thickness. The characteristic values for these structural parameters vary from one natural fibre to another (Tab. 2.1.2 and Tab. 2.1.3).

The spiral angle (Tab. 2.1.2) of the fibrils and the content of the cellulose (Tab. 2.1.3), determine generally the mechanical properties of the cellulose based natural fibres [18]. Due to their biological origin, cellulose fibres display a unique structural hierarchy: they are composed of an assembly of microfibrils, which in their turn consist of a number of cellulose molecules.

The density of cellulose is approximately 1.5 g/cm^3, so it is then possible to compare its mechanical performance (strength and Young's modulus) with those of other engineering material. We can conclude that cellulose is a high-performance material, comparable with the best fibres technology can produce.

The fibre properties and fibre structure are influenced by many conditions and vary according to their area of growth, its climate and the age of the plant. Further, the technical decomposition of the fibre is another important factor which determines the structure and the characteristic values of the fibre as well [18].

Tab. 2.1.2
Structure parameters of different cellulose base natural fibres [18]

Fibre	Spiral angle [°]	Cross-sectional area A.10^2 [mm^2]	Cell-length L [mm]	L/D-ratio (D is the cell diameter) [-]
from footstalks				
Jute	8.00	0.12	2.30	110
Flax	10.00	0.12	20.00	1687
Hemp	6.20	0.06	23.00	960
Ramie	7.50	0.03	154.00	3500
from leaves				
Sisal	20.00	1.10	2.20	100
Pineapple	14.00	–	–	–
from fruits				
Coir	41.00–45.00	1.20	3.30	35

Tab. 2.1.3
Chemical composition of different cellulose based natural fibres [18]

Fibre	Cellulose [wt. %]	Lignin [wt. %]	Hemicellulose [wt. %]	Pectin [wt. %]	Wax [wt. %]	Water [wt. %]
from footstalks						
Jute	61.00–71.50	12.00–13.00	13.60–20.40	0.20	0.50	12.60
Flax	71.00	2.20	18.60–20.60	2.30	1.70	10.00
Hemp	70.20–74.40	3.70–5.70	17.90–22.40	0.90	0.80	10.80
Ramie	68.60–76.20	0.60–0.70	13.10–16.70	1.90	0.30	8.00
Kenaf	31.00–39.00	15.00–19.00	21.50	–	–	–
from leaves						
Sisal	67.00–78.00	8.00–11.00	10.00–14.20	10.00	2.00	11.00
Pineapple	70.00–82.00	5.00–12.00	–	–	–	11.80
Henequen	77.60	13.10	4.00–8.00	–	–	–
from seeds						
Cotton	82.70	–	5.70	–	0.60	–
from fruits						
Coir	36.00–43.00	41.00–45.00	0.15–0.25	3.00–4.00	–	8.00

Climatic conditions, age and the digestion process influence not only the structure of fibres but also the chemical composition. With the exception of cotton, the components of natural fibres are cellulose, hemicellulose, lignin, pectin, waxes, water and water soluble substances, with cellulose, hemicellulose and lignin as the basic components with regard to the physical properties of the fibre [18].

2.2 Polymers as a Matrix

Besides the fibres, also the matrix strongly influences properties of the resulting composite system. Natural fibres can be used as reinforcements in both thermoset and thermoplastic matrices. At the moment, materials with conventional thermoset binders such as epoxy resin (EP) correspond to the requirements for higher performance applications. They provide sufficient mechanical properties, in particular stiffness and strength, at acceptably low price levels [18].

Epoxy resins are widely used in industrial applications, such as adhesives, bonding, construction materials (flooring, paving, and aggregates), composites, laminates, coatings, electronics, air- and spacecraft industries, textile finishing, leisure goods and so on. Due to their excellent mechanical and chemical properties, EPs are also one of the important materials used as the matrices for fibre reinforced plastics. Recently, instead of synthetic fibres, the use of natural cellulose fibres as reinforcements in polymer composites has gained popularity in engineering applications. Various researchers have investigated the strengthening effects on the plant fibres embedded in polyolefins, polystyrene, polyester and epoxy resin matrices [18–24].

Epoxy resins are polyether resins containing more than one epoxy group capable of being converted into the thermoset form. These resins, under curing, do not create volatile products in spite of the presence of a volatile solvent. The epoxies may be named as oxides, such as ethylene oxides (epoxy ethane), or 1,2-epoxide. The epoxy group also known as oxirane contains an oxygen atom bonded with two carbon atoms, which in their turn, are bound by separate bonds as shown in Figure 2.2.1. [20].

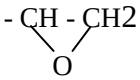


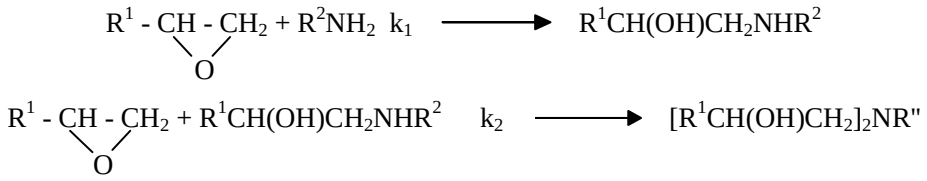
Fig. 2.2.1. Oxirane epoxy group contains an oxygen atom bonded with two carbon atoms.

The curing of the epoxy group takes place either between the epoxide molecules themselves or by the reaction between the epoxy group and other reactive molecules with or without the help of the catalyst. The former is known as homopolymerisation, or corrective curing. The latter is an addition or catalytic curing reaction. The both reactions result in coupling, as well as in crosslinking.

Although a great variety of curing agents (hardeners) based on amines, amides, phenols, thiols, carboxylic acids, and acid anhydrides exist, the number of hardeners available for

high-performance applications and prepreg manufacture in particular is limited. The curing agent must have latent reactivity for the resulting resin and prepreg to possess acceptable out-time (good tack and drape, generally for a minimum of 10–14 days at ambient temperature), and for the resulting cured system to have both a high glass transition temperature (T_g) and a maximised resin modulus [20–22].

Primary and secondary amines are widely used to cure epoxy resins. The reaction between the oxirane group of the epoxy resin with primary amines is shown in Fig. 2.2.2.



k_1, k_2–velocity constats of reaction
R^1, R^2, R" – organic functional groups

Fig. 2.2.2. Scheme of instant chemical reaction.

The curing of epoxy resins is an exothermic process, resulting in production of limited size molecules, having molecular weights of a few thousands. Epoxy resins have a very wide molecular weight distribution. This can be estimated by comparing the weight average, molecular weight (M_w) and number average molecular weight (M_n) values. The greater the difference is, the wider the distribution is. Epoxy resins are noncrystalline, and cured resin finds its structural applications below the heat distortion or T_g [18, 20–22].

In comparison with composites based on thermoplastic polymers such as polypropylene (PP), thermoset compounds have a superior thermal stability and lower water absorption. However, the demand for improved recycling concepts and alternative processing techniques are expected to result in a substitution of the thermoset polymers by thermoplastic polymers.

Composites fabricated from thermoplastic materials typically have a longer shelf life, higher strain to failure, faster consolidate and retain the ability to be repaired, reshaped and reused. However, these materials frequently suffer from a lack of adequate fibre-matrix adhesion. In addition, the use of thermoplastics introduces the problem of adequate fibre penetration. Thermoplastic polymers do not undergo chemical reactions, like thermosets which during their curing cross-link the polymer molecules, but only physical changes. Thermoplastics also can react with the cellulose of the fibres. Thermoplastic melts, as opposed to thermosetting resins and they have a substantially higher viscosity. Thermoplastic matrices must be able to withstand high temperatures in order to affect a sufficient reduction in viscosity. Additional problems caused by the high matrix viscosity during consolidation include de-alignment of reinforcing fibres during consolidation as well as the introduction of voids within the final composite product [25]. A common problem associated with these composite systems is also a poor interfacial adhesion between the low melting, non-polar and hydrophobic matrix material and the hydrophilic filler, resulting in poor mechanical properties of the final material. All these

problems can be solved by appropriate composite fabrication and arrangement procedures. General parameters affecting the properties of polymer composites include:

- the properties of the additives (inherent properties, size, shape);
- the composition;
- the interaction of components at the phase boundaries, which is also associated with the existence of a thick interface, known also as the interphase; which, considered a separate phase, controlling adhesion between the components;
- the method of fabrication.

Polyolefins are at the top of the list of commodity polymers, accounting for 90 % of all plastics manufactured. They are manufactured from petroleum-based feedstocks. Polyethylene (Fig. 2.2.3.), for example, is polymerised from the monomer compound ethylene, $CH_2=CH_2$ where the = symbol indicates a double bond. Double bond is shorter and stronger in a thermodynamic sense but it is more chemically reactive compared to a single bond. When ethylene is polymerised the double bond is replaced with two single bonds, one of which attaches to another ethylene monomer in the polymer chain. Single bonds between carbon atoms are difficult to break (i.e. they are stable). In part, polyethylene owes its stability to this uninterrupted string of carbon-carbon single bonds. Polyolefins are generally inexpensive and their physical properties, such as melting point, strength, and resistance to a lot of chemicals, are useful for a wide range of applications. It is their favourable cost-performance ratio that makes them the commodity leaders.

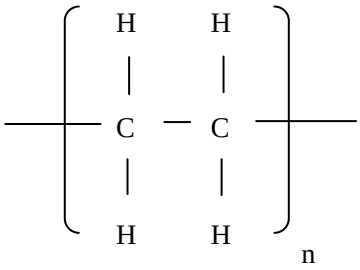


Fig. 2.2.3. Polymer chain of polyethylene (PE).

Polypropylene (Fig. 2.2.4.) differs chemically from polyethylene only in having a side chain group attached to every other carbon atom; in the case of PP, the side chain is a methyl group (CH_3) which causes stiffening and less stability with regard to oxidation. The backbone chains of the two polymers are the same. Polypropylene is an economical material that offers a combination of outstanding physical, chemical, mechanical, thermal and electrical properties not found in any other thermoplastic.

Polypropylene provides excellent resistance to organic solvents, degreasing agents and electrolytic attack. It has a lower impact strength, but its working temperatures and tensile strength are superior to low or high density polyethylene. With respect to polyethylene it is characterised by lower mass, low moisture absorption rate and is resistant to staining. This is a tough, heat-resistant, semi-rigid material, ideal for the transfer of hot liquids or gases. It is recommended for vacuum systems, higher heats and pressures. It has excellent resistance to acids and alkalines, but poor resistance to aromatic, aliphatic and chlorinated solvents.

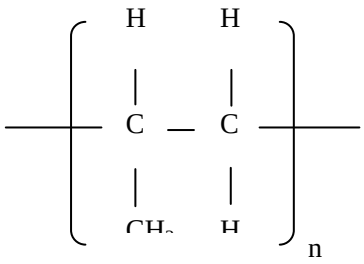


Fig. 2.2.4. Polymer chain of polypropylene (PP).

Polyethylene and polypropylene are resistant to environmental degradation, even in compost environment they can last many years. Polyethylene and polypropylene do degrade in the environment by oxidation. Natural daylight can accelerate the oxidation, giving rise to photo-oxidation (photodegradation). The carbon-carbon chains are broken, and the plastic will become brittle and eventually disintegrate. The degradation rate is however, very slow (nonetheless, anti-oxidation stabilisers still are added to polyethylene and polypropylene to prolong their useful lifetime).

Many polymers are also found abundantly in nature. Natural polymers tend to be degradable because organisms have evolved enzymes to attack them. Attention has reasonably turned to such polymers as potential feedstocks for compostable plastics. These manufactured biopolymers are inherently biodegradable, and as they are made from renewable resources they have the additional benefit of not depleting fossil resources [24, 26].

It is not easy to decide how to classify biodegradable polymers. They can be sorted according to their chemical composition, synthesis method, processing method, economic importance, application, etc. Each of these classifications provides different and useful information. In the present overview, we have chosen to classify biodegradable polymers (hereinafter called biopolymers) according to their origin into two groups: natural polymers, polymers coming from natural resources and synthetic polymers, polymers synthesised from natural oil.

From the chemical point of view, biopolymers of natural origins can be divided into six sub-groups:

- polysaccharides (e.g., starch, cellulose, lignin, chitin);
- proteins (e.g., gelatine, casein, wheat gluten, silk and wool);
- lipids (e.g., plant oils including castor oil and animal fats);
- polyesters produced by micro-organism or by plants (e.g. polyhydroxyalcanoates, poly-3-hydroxybutyrate);
- polyesters synthesised from bio-derived monomers (polylactic acid);
- a final group of miscellaneous polymers (natural rubbers, composites) [27, 28].

Biopolymers from mineral origins include four sub-groups:

- polyvinylalcohols;
- aliphatic polyesters (e.g., polyglycolic acid, polybutylene succinate, polycaprolactone);

- aromatic polyesters or blends of the two types (e.g., polybutylene succinate terephthalate);
- modified polyolefins (polyethylene or polypropylene with specific agents sensitive to temperature or light) [28].

Following table 2.2.1 shows another, a little bit more complicated dividing of bio-polymers.

Tab. 2.2.1
Classification of biopolymers [29]

Renewable Resource-based	Microbial synthesised	Petro-based synthetic	Petro-Bio (Mixed) Sources
PLA Polymer (From Corn)	Polyhydroxy alkanoates (PHAs)	Aliphatic polyester	Sorona
Cellulosic plastics	Polyhadoxybutyrate co-valerate (PHBV)	Aliphatic-aromatic polyester	Biobased polyurethane
Soy-based plastics		Polyesteramides	Biobased epoxy
Starch plastics		Polyvinyl alcohol	Blends etc.

Vinyl polymers, with few exceptions, are generally not susceptible to hydrolysis. Their biodegradation, if it occurs at all, requires an oxidation process, and most of the biodegradable vinyl polymers contain an easily oxidisable functional group. Approaches to improve the biodegradability of vinyl polymers often include the addition of catalysts to promote their oxidation or photooxidation, or both. The incorporation of photosensitive groups, e.g. ketones, into these polymers has also been attempted.

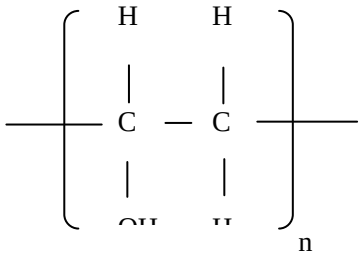


Fig. 2.2.5. Polymer chain of polyvinyl alcohol (PVA).

Polyvinyl alcohol (PVA) (Fig. 2.2.5.) is the most readily biodegradable of vinyl polymers. It is readily degraded in waste-water-activated sludges. The microbial degradation of PVA has been studied, as well as its enzymatic degradation by secondary alcohol per-oxidases isolated from soil bacteria of the Pseudomonas strain. It was concluded that the initial biodegradation step involves the enzymatic oxidation of the secondary alcohol groups in PVA to ketone groups. Hydrolysis of the ketone groups results in chain cleav-age. Other bacterial strains, such as Flavobacterium and Acinetiobacter were also effec-tive in degrading PVA [30].

PVA can form complexes with a number of compounds and has been used in the detoxification of organisms. When it is used in a low molecular weight form, i.e. below 15 000, it can be eliminated from organisms by glomerular filtration. PVA has also been used as a polymer carrier for pesticides and herbicides [31, 32].

2.3 Fibre-matrix Adhesion

Adhesion between fibre and matrix is widely considered a necessary condition to ensure good composite mechanical properties. If there is no adhesion between the two components, the composite will respond as if it were the bulk matrix material with voids retaining the shape of the included fibres (at low strains). At higher strains, Poisson's effect can bring mechanical friction forces between the fibre and matrix phase, thus causing the fibres to bring about a greater influence in material properties.

Three general theories can be used to describe the adhesive interaction between two surfaces:

- mechanical interlocking;
- inter-diffusion;
- adsorption and surface reaction [33].

First mechanism of adhesion occurs when a porous or roughly surfaced substrate is brought into contact with a surface that is able to flow and fill the projections of the rough surface. Once the surfaces fully solidify, a mechanically interlocked bond is created [33].

When it may be possible for molecules of one surface to diffuse into the bulk of another surface and set up an interphase, an inter-diffusion adhesive interaction occurs. This interphase represents the elimination of the joining surface and replaces it with a relatively smooth gradient from one bulk material to the other. Depending on the affinity of the molecules toward each other, the interphase may be thin (50–100 nm) as in the case of most polymers or relatively thick (10 µm) [33].

Adhesion by adsorption and surface reaction proceeds by the chemical attraction of specific sites by both of the surfaces to be joined [33]. These are frequently due to Van der Waals forces, ionic interactions, or strong covalent interactions. In this type of adhesive interaction, the water absorption of one surface by a liquid is particularly important – namely, the surface energy of the solid, the surface tension of the liquid and the viscous behaviour of the liquid. Wetting of a solid by a liquid is a precursor to adhesion, however, it is not a sufficient condition in forming a strong adhesive joint.

Adhesion in thermoplastic composite systems is usually enhanced using fibre surface treatments. There are several possibilities:

- surface treatment (e.g. plasma, silanisation);
- coupling and compatibilising agents (e.g. maleic anhydride, benzoylperoxide);
- change of fibres morphology (e.g. milling, cutting).

Reinforcing fillers are characterised by aspect ratio α, defined as the ratio of length to diameter for a fibre, or the ratio of diameter to thickness for platelets and flakes.

A useful parameter for characterising the effectiveness of filler is the ratio of its surface area A, to its volume V, which needs to be as high as possible for effective reinforcement.

Figure 2.3.1. shows relation between area/volume ratio *A*/*V* and aspect ratio α for fibres and for platelets [34].

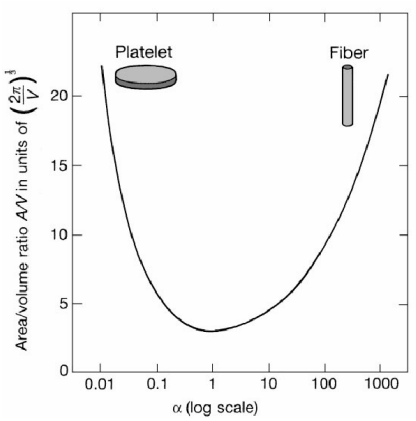


Fig. 2.3.1. Surface area-to-volume ratio *A/V*, of a cylindrical particle plotted versus aspect ratio α = l/d [34].

In developing reinforcing fillers, the aims of process or material modifications are to increase the aspect ratio of the particles and to improve their compatibility and interfacial adhesion with the chemically dissimilar polymer matrix. Such modifications may enhance and optimise not only the primary function of the filler (in this case its use as a mechanical property modifier), but may also introduce or enhance additional functions. Table 2.3.1 shows particle morphology of different type of fillers.

Tab. 2.3.1
Particle morphology of fillers

Shape	Aspect ratio	Examples
Cube	1	Feldspar, calcite
Sphere	1	Glass spheres
Block	1–4	Quartz, calcite, silica, barite
Plate	4–30	Kaolin, talc, hydrous alumina
Flake	50–200++	Mica, graphite, montmorillonite nanoclays
Fibre	20–200++	Glass fibres, wood fibres, asbestos fibres, carbon fibres, carbon nanotubes

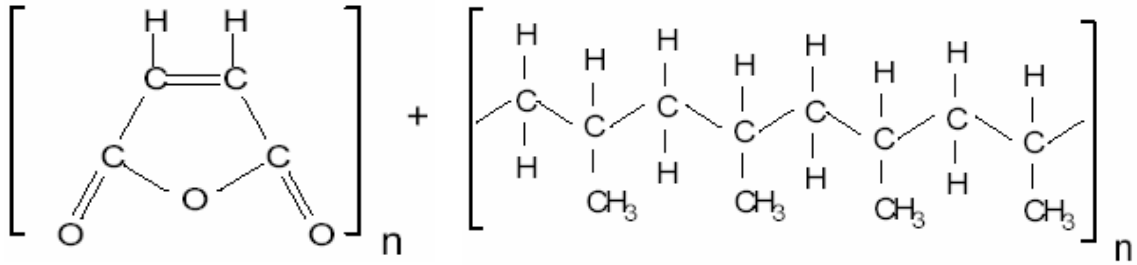
++ means that the aspect ratio is 200 and more

The modification of the surface of cellulose microfibrils to make them compatible with non-polar polymers has been attempted. In some approaches, corona or plasma discharges have been used. In other attempts, the adhesion of hydrophilic cellulose to hydrophobic polymer matrices has been increased by the use of coupling agents. Interaction of cellulose with surfactants has been another way to stabilise cellulose suspensions into non-polar systems. Such stabilisation was also achieved with surface grafting or derivation, figure 2.3.2. shows an example of grafting maleic anhydride with polypropylene on cellulose chain. In the latter case, the challenge has been to keep the integrity of the core of the cellulose microfibrils while modifying only the polarity of their skin [1, 12, 35–37].

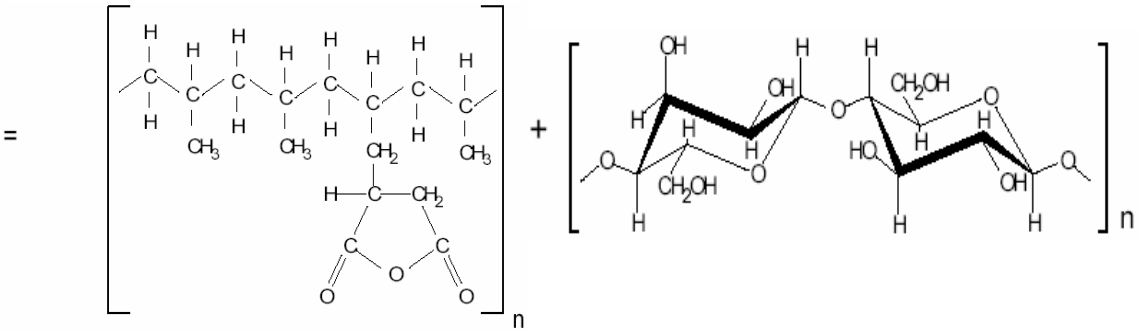
The inherent polar and hydrophilic nature of the lignocellulosic fibres and the non-polar characteristics of the polyolefins result in difficulties in compounding/blending the fibres and matrix. Maleic anhydride (MA) grafted polypropylene (MAPP) has been shown to function efficiently as a coupling agent for plant fibres – PP systems. This system was chosen because of low melting temperature of the polypropylene and that's why it is suitable for natural fibres. The maleic anhydride present in the MAPP provides polar interactions such as acid-base interactions and can covalently link the hydroxyl groups on the lignocellulosic fibre. It is reported that due to thermodynamic segregation, the MAPP gets localised on the cellulosic fibre surface in a PP matrix during the processing stage [38, 39].

The interactions between non-polar thermoplastics such as PP and any coupling agent, such as MAPP, are predominantly caused by chain entanglement. Stresses applied to one chain can be transmitted to other entangled chains and are distributed among many chains. These entanglements function like physical cross-links that provide some mechanical integrity up to, and above, the T_g, but become ineffective at much higher temperatures. When polymer chains are very short, there is little chance of entanglements between chains and they can easily slide past one another. When the polymer chains are longer, entanglement between chains can occur, chain slippage becomes more difficult, and the viscosity of the polymer becomes higher. A minimum chain length or a critical molecular weight (M_e) is necessary to develop these entanglements, and a typical polymer has a chain length between entanglements equivalent to a M_e varying from 10 000 to about 40 000. The M_e varies, depending on the structure of a polymer. For example, linear polyethylene has a M_e for entanglements of about 4 000, while for polystyrene, the M_e is about 38 000. Factors such as the presence of hydrogen bonding or side chains that affect the glass transition temperature of the polymer will also affect the M_e of the polymer melt. It is also important to note that the fibre surface is likely to act as a boundary and restrict the mobility of the polymer molecules, and the minimum entanglement lengths (M_e) will vary according to the fibre surface characteristics.

A maleic anhydride grafted PP that has a high MA content coupled with a relatively high molecular weight has resulted in efficient composites. That MAPP is reported to have a M_n of 20 000, a M_w of 40 000 and was about 6 % by weight of maleic anhydride. Any free anhydride present in the MAPP can complicate the understanding of the characteristics and function of the MAPP on the properties of the fibre – matrix interphase. The free MA may preferentially bond to available -OH sites on the fibre and reduce the interaction between the MAPP and the fibre. Furthermore, free MA bonded to the fibre surface can change the surface energetic of the fibre surface. Use of a MAPP with higher molecular weights, but lower MA contents than the MAPP mentioned earlier, result in composites with lower properties. Theoretically, extremely long chains of MAPP with substantial amounts of grafted MA would be an ideal additive in plant fibres – PP composites, creating both covalent bonding to the fibre surface and extensive molecular entanglement to improve properties of the interphase. However, extremely long chains may reduce the possibility of migration of the MAPP to the fibre surface because of the short processing times. If the M_w of the MAPP is too high, the MAPP may entangle with the PP molecules so that the polar groups on the MAPP have difficulty "finding" the -OH groups on the fibre surface [38, 39].



Maleic Anhydride (MA) Polypropylene (PP)



Maleic Anhydride Grafted Polypropylene (MAPP) Cellulose

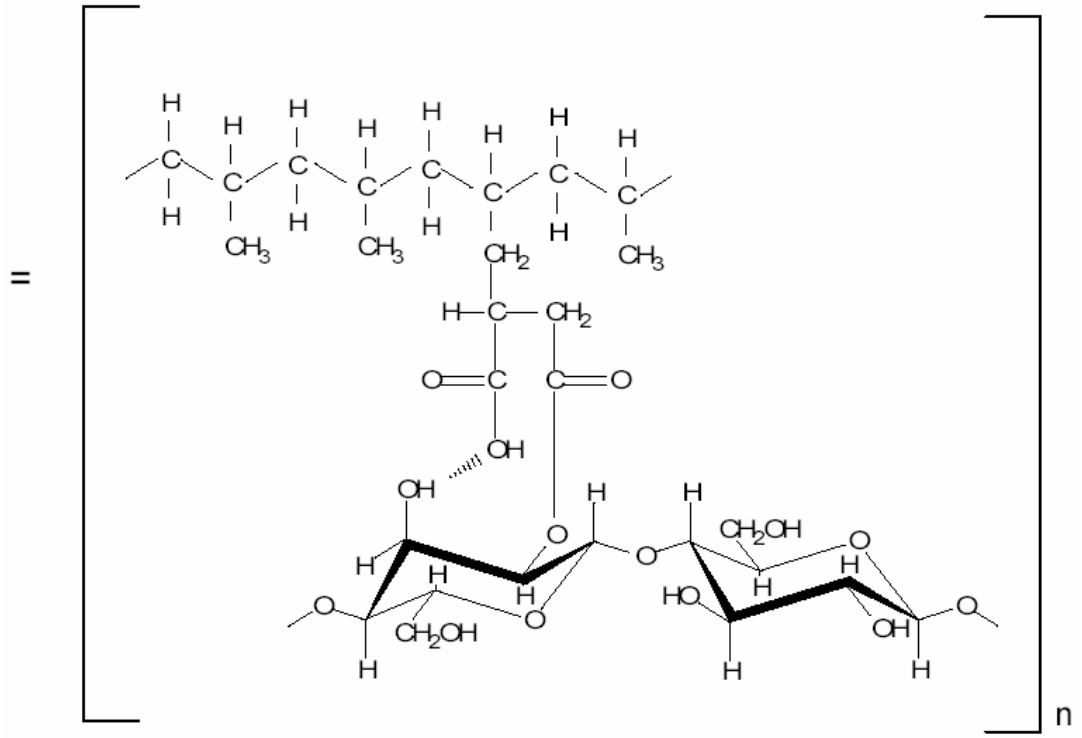


Fig. 2.3.2. Chemical bonding of maleic anhydride grafted polypropylene on cellulose chain [40].

As follows from the above review, a good adhesion between the fibres and the matrix is prerequisite for optimal load transfer from the matrix into the fibres for all composites and the knowledge of the fibre surface properties will help to optimise the interactions between the fibres and the matrix. Although the chemical treatments of fibre surfaces have been somewhat successful in improving the interfacial bonding, there are unresolved pollution problems related to the disposal of chemicals after treatment, plus the high cost of chemical treatment.

A new approach to the modification of natural fibre surfaces offers plasma treatment. Plasma technologies present an environmentally friendly and versatile way of treating natural plant fibres in order to enhance a variety of properties such as water absorption, liquid repellency, dyeability and coating adhesion. These technologies are suitable for modifying the chemical structure as well as the topography of the surface of the material. Cold plasma techniques are dry, clean processes without environmental concerns. Plasma can be defined as partially ionised gas that has a collective behaviour. One of the main advantages of this approach is that the modification is confined only to the surface of the materials without interfering with their bulk properties. Energetic species present in the discharge, such as electrons, ions, free radicals and photons, have energies high enough to alter all chemical bonds in the surface layers of natural polymeric substrates. Proper selection of starting compounds and external plasma parameters (e.g. power, pressure and treatment time) allow creation of desired characteristics on lignocellulosic substrate surfaces [40–42]. In a cold plasma treatment system, depending on the type and nature of the gases used, a variety of surface modifications can be achieved. Surface energy can be increased or decreased, cross-linking can be introduced, and reactive free radicals and groups can be produced. In the case of wood surface activation, this process increases the amount of aldehyde groups [18].

For the treatment of natural fibres this means that hydrophilicity as well as hydrophobicity may be achieved; moreover, both the surface chemistry and the surface topography may be influenced to result in improved adhesion or repellency properties as well as in the confinement of functional groups to the surface [18, 41–44].

2.4 Nanofibrecomposites

Importance of the aspect ratio (ratio of length of fibre to its diameter) of fibrous filler follows from the previous text. Nanofibres are the most suitable type of filler from this point of view – it is possible to produce them artificially or they can be found in nature.

2.4.1 Artificial Nanofibres

Nanofibres and nanotubes of carbon and other materials are the most fascinating nanomaterials playing an important role in nanotechnology today. Their unique mechanical,

electronic, and other properties are expected to result in revolutionary new materials and devices (Tab. 2.4.1). They are used for several value added applications such as medical, filtration, barrier, wipes, personal care, composite, garments, insulation, and energy storage. Special properties of nanofibres make them suitable for a wide range of applications from medical to consumer products and from industrial to hightech applications for aerospace, capacitors, transistors, drug delivery systems, battery separators, energy storage, fuel cells, and information technology [45].

Carbon nanotubes are one of the most commonly mentioned building blocks of nanotechnology. With one hundred times the tensile strength of steel (Tab. 2.4.2), thermal conductivity better than all but the purest diamond, and electrical conductivity similar to copper, but with the ability to carry much higher currents, they seem to be a wonder material [46–48].

In fact nanotubes come in a variety of forms: long, short, single-walled, multi-walled, open, closed, with different types of spiral structure, etc. Each type has specific production costs and applications. Some have been produced in large quantities for years while others are only now being produced commercially with decent purity and in quantities not greater than a few grams.

The term nanotube is normally used to refer to the carbon nanotube, which has received enormous attention from researchers over the last few years and promises, along with close relatives such as the nanohorn, a host of interesting applications. There are many other types of nanotube and nanofibre, from various inorganic kinds, such as those made from boron nitride, to organic ones, such as those made from self-assembling cyclic peptides (protein components) or from naturally-occurring heat shock proteins (extracted from bacteria that thrive in extreme environments). However, carbon nanotubes excite the most interest, promise the greatest variety of applications, and currently appear to have by far the highest commercial potential [46].

Carbon nanotubes were synthesised in a carbon arc-discharge in 1991. Since then, other authors have reported the growth of carbon nanotubes from an arc-discharge [49] and other methods have been developed to synthesise nanotubes. Carbon nanotubes have also been produced by vaporisation processes using lasers, electron beams and solar energy. Catalyctic pyrolysis and chemical vapour deposition of hydrocarbons are now widely used for carbon nanotube growth as simple and efficient methods [49–58]. In addition to carbon nanotubes, similar methods have been used for the synthesis of carbon nanofibres, also known as carbon filaments since the early 1950s. Carbon nanofibres can be grown using catalytic decomposition of hydrocarbons over transition metal particles such as iron, cobalt, nickel, zinc and their alloys at temperatures ranging from 500 to 1 000 °C [54]. Microwave plasma enhanced chemical vapour deposition (PECVD) process, used for the preparation of diamond and diamond-like carbon films, has been recently developed successfully for the growth of carbon nanotubes and carbon nanofibres. Recently the first evidence of carbon nanofibres growth at room temperature using radio frequency PECVD have been published. Nanotubes and nanofibres need not be of carbon alone and various other elements (e.g. boron) have been incorporated into nanotubes and nanofibres [59, 60].

Generally, polymeric nanofibres are produced by an electrospinning process. Electrospinning is a process that spins fibres of diameters ranging from 10 nm to several 100 nano-

Tab. 2.4.1
Properties of nanoreinforcement [48]

Property	Exfoliated Clay	Carbon Nanotube (NT)	Exfoliated boron nitride NT	Cellulose Nanowhisker	Graphite Nanoplatelet
Physical structure	platelet ~ (1 x 100) nm	cylinder ~ (1 x 100) nm	layer	needle/whisker	platelet ~ (1 x 100) nm
Chemical structure	SiO_2, Al_2O_3, MgO, K_2O, Fe_2O_3	graphene (chair, zigzag, chiral)	boron nitride	cellulose	graphene
Interactions	hydrogen bond dipole – dipole	Π – Π	hydrogen bond	hydrogen bond	Π – Π
Tensile modulus	0.17 TPa	(1.00–1.70) TPa	~ 1.00 TPa	~ 130 GPa	~ 1.00 TPa
Tensile strength	~ 1.00 GPa	180 GPa	?	10 GPa	~ (10–20) GPa
Electrical resistivity	10^{10}– 10^{16} Ωcm	~ 50 x 10^{-6} Ωcm	insulator	10^{10}– 10^{16} Ωcm	~50 x 10^{-6} Ωcm∥ ~ 1 Ωcm ⊥
Thermal conductivity	6.7 x 10^{-1} W/mK	3 000 W/mK	conductor	insulator	3 000 W/mK∥ 6 W/mK ⊥
Thermal exp. coefficient	(8–16) x 10^{-6}	-1 x 10^{-6}	~ 1 x 10^{-6}	(8–16) x 10^{-6}	-1 x 10^{-6}∥ 29 x 10^{-6} ⊥
Density	2.8–3.0 g/cm^3	1.2–1.4 g/cm^3	~ 2.0 g/cm^3	1.2 g/cm^3	~ 2.0 g/cm^3

Tab. 2.4.2
Some mechanical properties of carbon nanotubes as compared to conventional materials [47]

Property	Graphite Crystal	Carbon Fibres	MWNT*	SWNT**	Steel
Tensile Strength [GPa]	100	3–7	300–600	300–1 500	0.40
Elastic Modulus [GPa]	1 000	200–800	500–1 000	1 000–5 000	200.00
Specific Strength [GPa cm^3/g]	50	2–4	200–300	150–750	0.05
Specific Modulus [GPa cm^3/g]	500	100–400	250–500	500–2500	26.00
Strain to Failure [%]	10	1–3	20–40	20–40	25.00

* multi-walled nanotube
** single-walled nanotube

metres (continuous nanofibres). This method has been known since 1934 when the first patent on electrospinning was filed. This technology enables production of continuous nanofibres from polymer solutions or melts in high electric fields. A thin jet of polymer liquid is ejected, elongated, and accelerated by the electric forces. The jet undergoes a variety of instabilities, dries, and is deposited on a substrate as a random nanofibre mat. The interest in the electrospinning and electrospun nanofibres has been growing steadily since the mid-1990s, triggered by potential applications of nanofibres in the nanotechnology. Fibre properties depend on field uniformity, polymer viscosity, electric field strength and DCD (distance between nozzle and collector). Although diameters as small as 3 to 5 nanometres were reported, nanofibres smaller than about 50 nm in diameter cannot currently be produced uniformly and repeatedly for most materials systems [61–66].

Another technique for producing polymeric nanofibres is spinning bi-component fibres such as Islands-In-The-Sea fibres in 1-3 denier filaments with from 240 to possibly as

much as 1 120 filaments surrounded by dissolvable polymer. Dissolving the polymer leaves the matrix of nanofibres, which can be further separated by stretching or mechanical agitation. The most often used fibres in this technique are nylon, polystyrene, polyacrylonitrile, polycarbonate, PEO, PET and watersoluble polymers. The polymer ratio is generally 80 % islands and 20 % sea. The resulting nanofibres after dissolving the sea polymer component have a diameter of approximately 300 nm. Compared to electrospinning, nanofibres produced with this technique will have a very narrow diameter range but are coarser [62].

However, these nanomaterials, produced mostly by synthetic bottom-up methods, are discontinuous that leads to difficulties with their alignment, assembly and processing into applications. Partly because of this, and despite considerable effort, a viable reinforced supernanocomposite is yet to be demonstrated. Advanced continuous fibres produced a revolution in the field of structural materials and composites in the last decades. Fibre properties are known to substantially improve with a decrease in their diameter. However, conventional mechanical fibre spinning techniques cannot produce fibres with diameters smaller than about 2 micrometres. Most commercial fibres are several times that diameter, owing to the trade-offs between the technological and economic factors [62].

The process of making nanofibres is quite expensive compared to conventional fibres due to low production rate and high cost of technology. In addition, the vapours emitting from solution while forming the web need to be recovered or disposed of in an environ-mentally friendly manner. This involves additional equipment and cost. The fineness of fibre and evaporated vapour also raises much concern over possible health hazard due to inhalation of fibres. Thus the challenges faced can be summarised as:

- economics;
- health hazards;
- solvent vapour;
- packaging, shipping, handling.

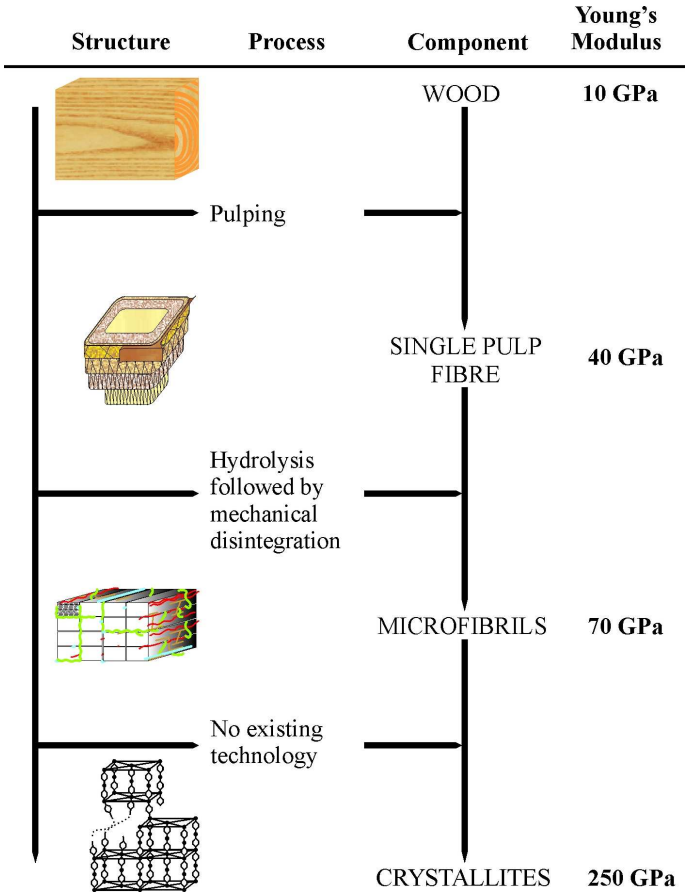
Because of its exceptional qualities there is an ongoing effort to strike a balance between the advantages and the cost [45].

Several types of nanoscale filler are already commercially important, including fillers based on carbon nanotubes and nanofibres. These nanofibres of diameter up to 200 nm are being produced as e.g. HILLS, Inc.; eSpin, Inc.; CNI, Inc; HELIX, Inc. [49–55].

2.4.2 Natural Fibres

Natural fibres can be processed in different ways to yield reinforcing elements having several mechanical properties. The elastic modulus of bulk natural fibres such as wood is about 10 GPa. Cellulose fibre with modulus up to 40 GPa can be separated from wood, for instance, by chemical pulping processes. Such fibres can be further subdivided according to hydrolysis followed by mechanical disintegration into microfibrils with the elastic modulus of 70 GPa. Theoretical calculations of the elastic modulus of cellulose chains have given values of up to 250 GPa, however, there is no technology availa-

ble to separate these from microfibrils (Fig. 2.4.1.) [23]. The best experimental estimate for the Young's modulus of cellulose (and, for that matter, for other linear polysaccharides in the cell walls) is approximately 130 GPa and strength of up to 7 GPa [10, 24]. This would give them a greater energy absorbing capability than the best synthetic fibres, e.g. Kevlar 149® fibres have a stiffness of 180 GPa and a strength of 3.4 GPa. The highest stiffness and strength measured for whole phloem fibre cells is 80 GPa and 2 GPa, respectively, for flax. However, these are composed of only 65 % cellulose [10], so strength and stiffness are, as expected, lower than that of cellulose microfibrils. In principle all plant cells, including those that are not elongated into fibres, could provide



high quality microfibrils for reinforced composite manufacturing.

Fig. 2.4.1. Correlation between structure, process, resulting component and Young´s modulus were redrawn after [33].

Cellulose can be used as a microfibrillar filler, which is accessible in terms of available amounts and preparation. They can be extracted from the biomass by a chemical treatment leading to purified cellulose, followed by a mechanical treatment in order to ob-

tain a homogeneous suspension due to the individualisation of the microfibrils. Composite materials with an acceptable level of dispersion should be processed mixing them with thermoplastics, water soluble polymers or latexes as the matrix. Indeed, after drying, cellulose microfibrils strongly interact through hydrogen bonds and cannot easily be dispersed again.

This hydrogen bonding is best exemplified in paper where these secondary interactions of the macrofibrils provide the basis of its mechanical strength. This may increase their manufacturing complexity. The dispersion level of cellulose fibres within a thermoplastic matrix is naturally subordinated to the processing technique used and to the physico-chemical nature of the matrix, but also to the fibre shape before adding to the polymer and to their interaction degree. The extraction step of cellulose microfibrils from the cell wall is therefore important in the final properties of such composites [16].

2.4.2.1 Methods of Cellulose Nanofibres Production

There are a lot of papers, which deal with possibilities of defibrillation of cellulose fibres in nano scale. The description of the most used methods reported in literature follows.

The kraft pulp in a 3 % water suspension was defibrillated in paper [5] by using a refiner and then passed through the micro-gap of a high-pressure homogeniser resulting in a large pressure drop causing shearing and impact forces in the pulp. The homogeniser treatment was repeated up to 30 times to obtain different degrees of microfibrillation. Then, the microfibrillated kraft pulp fibre was subjected to centrifugation to increase the solid content to 10 % (wet weight basis). Pulp fibres were defibrillated and branched to form a web-like structure, part of the pulp was reduced to 10 nm widths.

Hepworth and Bruce [10] made a composite to show that it is possible to exploit the benefits of the nanocomposite structure of cell walls without the need to completely separate the microfibrils from fragments of primary plant cell wall. These results showed that primary cell wall material could be used to make composites with useful and good properties. Possibility of microfibrils separation from cell wall material has been also demonstrated in this thesis. These extraction procedures involve harsh chemical and mechanical treatments that may significantly reduce the strength of the microfibrils. Fragments of plant cell wall were extracted from a vegetable parenchyma tissue and pressed together with PVA to form a composite sheet.

Swede root was the source of the cell wall material in this experiment. It is composed mostly of fluid filled parenchyma cells with some secondarily thickened and elongated vascular cells. Fresh root tissue was used as a base for preparation of a fine paste using a food processor. The wet paste was then suspended in 1 % detergent to destroy the lipid membranes and allow the cell contents to be extracted into the external fluid. After 2 h, the swede pulp was collected in a muslin cloth filter (50 μm pore size) and washed with distilled water for 1 h. The paste was then resuspended in 0.5 M HCl for 2 h at 50 °C to remove some of the pectins that hold cells together (in paper [16], solid residue was treated with dilute 0.05 M HCl for 1 h at 85 °C). The pulp was collected in a muslin cloth

filter and washed in distilled water, before being ground into a smooth paste by hand using a pestle and mortar. The paste was placed into a muslin bag between two metal plates and pressure was applied using a clamp to squeeze out more than 90 % of the water.

Producing microfibrils from sugar beet pulp, potato pulp and opuntia pulp are presented in several papers, a majority of them from Dufresne et al. [14–16, 30]. All these methods are very similar to each other.

A dried pulp was dispersed in water for 10 min with a blender at a concentration of 2 % w/w (the slurry was then poured on a 0.25 mm sieve and washed with water, to remove most of the remaining starch granules in papers [15] and [30]). The product was concentrated and resuspended in 2 % NaOH solution allowed the solubilisation of pectins and residual starch. The alkaline suspension was shaken for 2 h at 80 °C and then filtered and washed. A second extraction was performed under the same alkaline conditions and the alkali-insoluble product was bleached with sodium chlorite following the method of Wise et al. [67]. The resulting bleached product consisted essentially of individual parenchymal cell rests and vessels together with about 9 % minerals. Some of this mineral was removed by washing the rests of cell under running water on a 60 μm mesh nylon sieve. In papers [15] and [30], the resulting insoluble residue was bleached with a sodium chlorite $NaClO_2$. (After this bleaching treatment in a buffer medium – sodium acetate buffer, pH = 4.9 for 2.5 h at 70 °C and the cellulose residue was washed extensively with distilled water and freeze-dried in paper [15].)

The purified pulp was disrupted in a blender operated at 18 000 rpm for 15 min at a concentration between 1 % and 2 %. The pulp was heated up. The sample which had reached a temperature of 60 °C was immediately treated with a laboratory scale Manton-Gaulin homogeniser 15MR-8TBA (APV Gaulin Inc., Wilmington Mass). The sample was passed fifteen-time at a pressure of a 500 bars and the temperature was kept below 95 °C. A creamy suspension resulted that neither flocculated nor sedimented when diluted with water. Isolated cellulose microfibrils had about 2–4 nm in diameter [14] and the length was much higher (tens, sometimes hundreds of nm), leading to a practically infinite aspect ratio of the microfibril [12 – 16, 30].

The method of Dufrense et al. [14–16, 30] of separation microfibrils from sugar beet root tissue was not found to produce the required degree of breakdown of swede root tissue, so a similar procedure was developed but using longer mechanical processing stages and different equipment during the initial processing. The first two steps produced purified cell wall fragments in which the structure of the cellulose cell wall was maintained. The third processing stage of mechanical treatment produced fibrillated cell wall material, containing separated microfibrils [9].

First the root material had to be broken down to produce fragments of cell wall. The swede root was peeled to remove the waxy cuticle and epidermal layers that have thicker cell walls, and cut roughly into 10 mm cubes. 0.25 kg of these was placed in a laboratory blender with 0.5 l water and liquidised for 2 min. The material was passed over a 150 μm sieve and put into electrically driven mortar and pestle device, and processed for 3 h, by which time it had a smooth texture without visible lumps. The material was removed and cooked in a microwave oven for 3 min. This caused cells and pieces of

cells that were still attached to each other to separate, as a result of the solubilisation of pectin bonds. The cooked material was replaced in the mortar and pestle and processed for a further 0.5 h to complete the size reduction.

The second step was a chemical extraction which was performed to remove as much of the non-cellulose components of the wall as possible, i.e. pectins, hemicelluloses and proteins, so as to leave the cellulose fibrillar skeleton of the wall. To achieve this, the cell wall suspension from stage 1 was incubated and stirred with 2 % sodium hydroxide for 2 h at 80 °C, and passed over a 23 µm nylon sieve under vacuum. The filtrate was placed into a solution of sodium chlorite buffered to pH 4.9 with sodium acetate for 2 h at 70 °C and then washed with 5 l of water, to result in 38 g of purified cell wall material, with a dry matter content of about 4 %.

Last step was to separate the microfibrils in the cell wall fragments from each other, the purified cell wall material was further processed. A 2 % suspension of the purified cell wall material in water was passed through a homogeniser, in which the liquid and its suspended particles were pressurised to 500 bar and thus forced through an aperture so that the liquid was subjected to a high shear flow. The forces thus generated on the cell wall particles fragments were sufficient to separate some of the microfibrils. This material was cooled and kept at 2 °C until needed.

Three hours of grinding in a pestle and mortar reduced the swede tissue to fragments that range in size from 1 to 400 µm in diameter. The smallest particles are fragments of cell walls while the largest fragments are clusters of several cells. The additional cooking stage after the pestle and mortar treatment, followed by more grinding increases the number of smaller cell wall fragments in the range of 1–50 µm. Subsequent filtering through a 23 µm sieve removed particle of the size of individual cells or larger, leaving a paste that was found to be composed of cell wall fragments of less than 10 µm. No whole cells were observed. Examination of the fragments by light microscopy showed that there were equal numbers of fragments in both the 1–4 µm and the 6–9 µm range.

However, there were still many fragments of cell wall that had not been fibrillated. It was not possible to quantify the proportion of material separated. In a typical set of views, the amount of sample was too small to be representative and fibrils were often tangled together, so neither the size of microfibrils nor the proportion could be estimated with useful accuracy.

2.4.2.2 Patents

Many patents devoted to preparation of cellulose microfibrils have applied similar defibrillation methods of as described in the above mentioned articles but not all of them produce fibres in nanoscale. They use misnomer, most of the fibres are macrofibres. For example, preparation of microfibrils is reported in patents from textile industry [68–70], but these microfibrils are about 20 µm or less in diameter.

Also preparation of cellulose fibres of the length of thousands of nanometres or less long is known in papermaking, e.g., wood chips to a full chemical or semi-chemical proc-

ess for the purpose of separating the cellulose fibres therein from other naturally incident components. In such chemical process, the wood chips are cooked with suitable chemicals in an aqueous solution, usually at elevated temperatures and pressures. The object is to dissolve the naturally incident lignin and other extraneous compounds, leaving the cellulose intact and in fibrous form. The objective can be carried out to a commercially satisfactory degree [1, 35]. Without heating – the energy required to vaporise the water contained in lignocellulosic material is applied not by thermal external heating but using of microwave or radio wave radiation, at a frequency within the range from about 10 to about 300 000 MHz [2]. In this case the fibres are thousands of micrometres long.

Microfibrils sheets can be produced by forming a microfibril suspension into paper as described in literature [3]. Examples of usable methods include treatments using medium stirring mills, vibration mills, high-pressure homogenisers, stone mill grinding, and so on. Usable dispersion media are preferable water, ethylene glycol, methanol and ethanol. In consideration of paper production, fluidity, conditions in which microfibrils do not flocculate, etc., the concentration of the suspension is about 0.01 to 10.00 wt. %.

In patent [7], the process of the present invention involves simple but effective chemical and pressure mixing processes, such as homogenisation operation. The process yields refined cellulose products from any cellulose source, including even minor amounts of wood fibres as additives, but more preferably from harvest residue crop fibre and other crop waste fibre sources such as silage, stalks, leaf (including tree leaves), and the like. After dewatering, the microfibre or microfibrillated or highly refined cellulose formed a very hard solid material. Further investigation on the mechanical properties of samples indicated a potential for making materials similar to synthetic polymers that can be used in manufacturing industry.

The process is intended for the formation of compositions and comprises:

- providing a composition comprising non-wood cellulose fibre;
- mechanical reduction of the size of the cellulose fibre to less than 2 mm;
- reducing the binding effect of lignin on the microfibre content of the cellulose material to form a first fibre product (this is done by expanding the fibres into microfibre components, essentially breaking the binding action of the lignin on the microfibres, and/or by actual amount of lignin present in said composition comprising cellulose fibre);
- providing pressure of at least 2 MPa (up to 14 MPa or more) the fibre product while a liquid is present;
- removing pressure within a time interval, which will cause cellulose fibre to break down into a second fibre product comprising microfibres in liquid;
- optional hardening of second fibre product by removal of at least some of the liquid.

The process reduces the amount of lignin by weight of solids in fibre product to less than 1.00 % or down to essentially 0.00 %. The reduction of the amount of lignin is based upon controlling the relative ability of the fibres to be handled during subsequent processing. Larger amounts of lignin, such as the midrange of about 6 % by weight of fi-

bre, found in corn cellulose fibre composition, reduces the free moving action of individual fibres and subsequently the microfibres. The binding action and/or presence of lignin can reduce the surface expansion effect (e.g. the ratio of surface area after expansion as compared with the surface area before expansion) and reduces the ability of the microfibres to intertwine and entangle, and thus reduces the structural integrity and/or the final product.

The reduction of the amount of lignin is performed by a process gaining cellulose fibre with alkali metal hydroxide (e.g. aqueous sodium hydroxide) at temperature between 40 and 110 °C, with 100 °C being the presently practised operating temperature, or by an alcohol cooking system using 50 % aqueous ethanol cooking at 185 °C for 30 to 60 minutes.

The resulting fibre products of the process are termed “highly refined fibres”. These fibres should be clearly distinguished from the fibres produced by alternative technology discussed above. For example, with the milling of cellulose fibres, internal surface area reaches approximately 1.0 m^2/g with very fine milled fibres [7].

The invention [8] is focussed on the nanofibrils, which are embedded in the secondary cell wall. Those cellulose nanofibrils have diameter in the range of 5–60 nm and the length in thousands of nanometres. A method has been developed to manufacture those nanofibrils at a high yield from natural fibres.

A process for obtaining cellulose nanofibrils from natural fibres involves heating a pulp suspension to 80–90 °C, extracting the cellulosic material with an acid (dilute HCl of 1 M conc.) followed by the extraction of pulp with base (conc. less than 3 % wt./wt.), and then pouring liquid nitrogen into the pulp and keeping the sample in liquid nitrogen for 5–10 minutes to freeze the cell wall water and then applying high impact for breaking the cell walls and hence liberating the microfibrils from the secondary cell wall. The step is then followed by high pressure defibrillation by passing the 2 % w/w suspension of the liquid nitrogen crushed sample through high pressure defibrillator using PANDA 2K by NIRO SOAVI ® unit subjecting the treated suspension to a high pressure. The resulting suspension reaches more than an 18 % yield of nanofibrils entangled together.

2.4.3 Nanocomposites

Nanotechnology is now recognised as one of the most promising areas for technological development in the 21st century. In materials research, the development of polymer nanocomposites is rapidly emerging as a multidisciplinary research activity whose results could broaden the applications of polymers to the great benefit of many different industries.

These materials offer improvements over conventional composites in mechanical, thermal, electrical and barrier properties. Furthermore, they can reduce flammability significantly and maintain the transparency of the polymer matrix. (In the case of layered silicate – clay nanocomposites, loading levels of 2 % to 5 % of weight result in mechanical

properties similar to those found in conventional composites with 30 % to 40 % reinforcing material [71].)

These attractive characteristics already suggest a variety of possible industrial applications for polymer nanocomposites:

- automotive (gas tanks, bumpers, interior and exterior panels);
- construction (building sections and structural panels);
- aerospace (flame retardant panels and high performance components);
- electrical and electronics (electrical components and printed circuit boards);
- food packaging (containers and wrapping films).

Polymer nanocomposites represent a class of two-phase polymeric materials (thermoplastics, thermoset or elastomers) in which the size of the dispersed phase range on the nanometre length scale with small quantities. Similarly to the conventional fillers, nanofillers can be classified by their aspect ratio. Isodimensional nanofillers with nanometre sizes in all dimensions comprise precipitated or fumed silica, glass beads as well as silicon-titanium oxides and silsequioxanes prepared by sol-gel processes. Cellulose whiskers or carbon nanotubes are nanofillers with two dimensions in the nanometre scale. Plate-like fillers with one dimension on the nanolevel such as layered silicates form the third group of nanofillers. Polymer nanocomposites offer properties not yet attained with conventional filler technology. The dispersion of nanoscale particles leads to a substantial increase in the number of second-phase particles per volume of material compared to macroscale particles even at low loadings (usually below 5 wt. %). Almost the entire polymer is located at the interface of the nanofillers and thus the materials properties are dominated by the interfacial interactions. Moreover, the arrangement of the nanoparticles can strongly influence the properties. Spatial orientation of spherical, fibrous or plate-like nanoelements into one-, two- or three-dimensional arrays with varying degree of order leads to self-assembling superstructures with novel structure property relationships.

While natural or synthetic microfillers are used extensively to modify polymer properties, the use of performed nanofillers is rather limited because of dispersion problems and viscosity build-up relating to strong interparticle interactions [71].

There are some patents which describe preparation and processing of nanocomposites. Polymers, metals and ceramics are used as matrices of nanocomposite systems with several types of fillers. A lot of these patents deal with particulate inorganic filler. Clays [72–74], silicate and organophyllosiclicate [75–77] or graphite [78] are used in nanocomposites with polymer matrix.

3 Target of the Research Work

This research work is focused on investigation of utilisation of natural cellulose fibres and microfibres in composite systems with polymer matrices.

In order to characterise the selected systems, three main aims of studies were observed: defibrillation of natural cellulose fibres, measurement of water absorption of fibres and of complete composite systems, and measurement of mechanical properties (tensile strength and Young's modulus) of these composites. Three types of polymer matrix were selected: epoxy resin representing hydrophobic thermoset and from thermoplastic polymers hydrophobic polypropylene and hydrophilic polyvinyl alcohol. From the produced cellulose fibres bamboo, flax, hemp, and recycled paper were selected as filler.

The aim of the work is to obtain original basic research results in characterisation of mechanical properties of composite systems with hydrophilic natural cellulose fibres as a filler and hydrophobic or hydrophilic polymer matrices. Selection of the topics is based on the fact that defibrillated and nondefibrillated cellulose fibres in combination with degradable polyvinyl alcohol matrix could have potential of usage as fully biodegradable composite systems. Possibility of adhesion improvement between hydrophilic fibres and hydrophobic polypropylene matrix as mostly used thermoplastic is studied. Influence of various types of modification by solvents was observed – maleic anhydride grafted polypropylene as a coupling agent and oxygen or air plasma surface treatment of polymer. Characterisation of composite systems with widely used constructional thermoset epoxy resin is studied as supplementary research.

The goals of this PhD thesis are summarised into the following four sub-goals:

1. to suggest and develop a method of preparation of composite systems test pieces on polymer matrix base with natural cellulose fibres as a filler by using different techniques;
2. characterisation of mechanical properties and investigation of decisive factors influencing these properties;
3. characterisation of behaviour of produced composites with respect to water and humid environment;
4. to develop a defibrillation method of natural cellulose fibres and to verify possibilities of composite systems preparation with these fibres.

4 Materials

4.1 Fibres

4.1.1 Defibrillated Fibres

Cellulose fibres Cware F10.2 (Fig. 4.1.1.) with length up to 2 mm, produced by company CWA, Cellulosewerk Angelbachtal GmbH were used for defibrillation.

Two types of cellulose fibres from recycled paper (PSP fibres from company PSP Papierschaum AG) were used: PSP-grey, fibres from unbleached recycled paper and PSP-white, fibres from bleached recycled paper. Both types of fibres were in the same size as Cware F10.2 fibres – up to 2 mm (Fig. 4.1.2.).

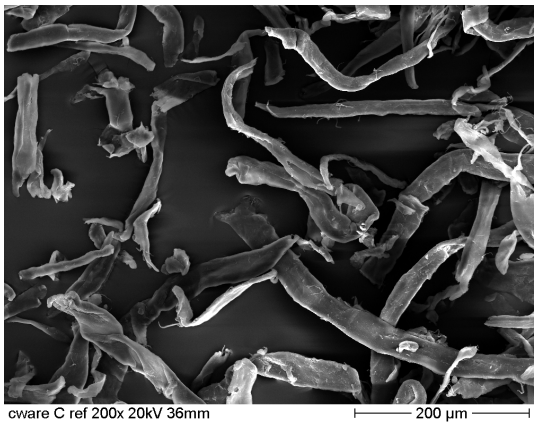


Fig. 4.1.1. Sample of Cware F10.2 cellulose fibres.

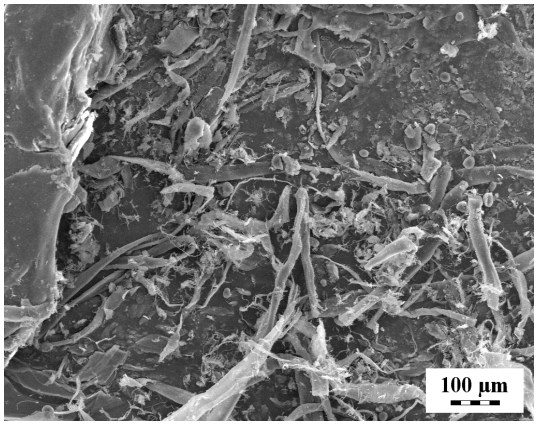


Fig. 4.1.2. Sample of unbleached PSP cellulose fibres from recycled paper.

4.1.2 Nondefibrillated Fibres

Nondefibrillated fibres were used to form composite systems with several types of polymer matrices. Recycled paper – PSP-grey cellulose fibres from company PSP Papierschaum AG were used as nondefibrillated filler, too.

Bamboo fibres (Fig. 4.1.3.) of technical quality produced by the company PMG Geotex GmbH. were also tested. Their length was up to 3.5 mm and diameter up to 0.5 mm. The density of these technical fibres was 1.5 g/cm³.

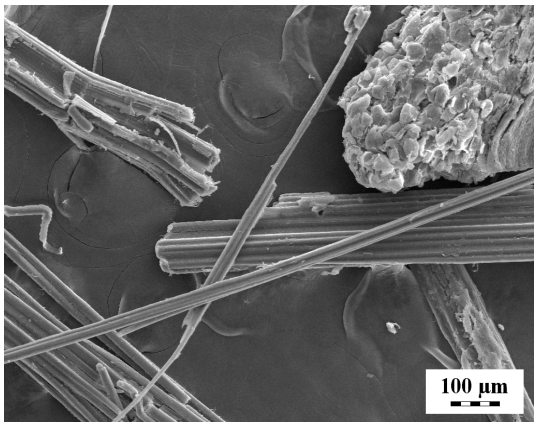
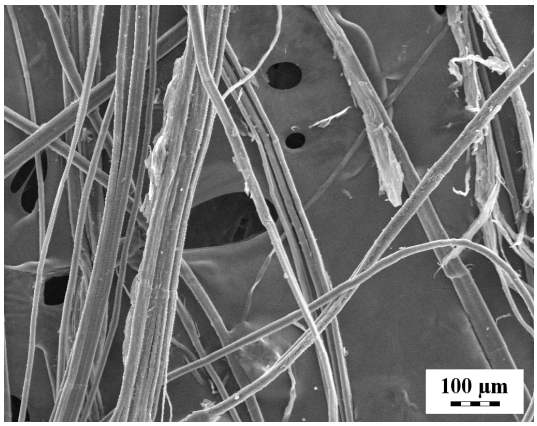


Fig. 4.1.3. Sample of bamboo fibres.

Flax fibres (Fig. 4.1.4.), from Holstein Flachs company, have brand name Konfektionierte Kurzfaser. These technical fibres had length up to 6 mm, diameter up to 0.4 mm



and density 1.4 g/cm³.

Fig. 4.1.4. Sample of flax fibres.

Technical hemp fibres (Fig. 4.1.5.) with name Superkurzfasern SKF2 were purchased from company BaFa GmbH. These fibres were up to 3 mm long, their diameter was up to 0.5 mm and density was the same as in the case of flax fibres, that were 1.4 g/cm³.

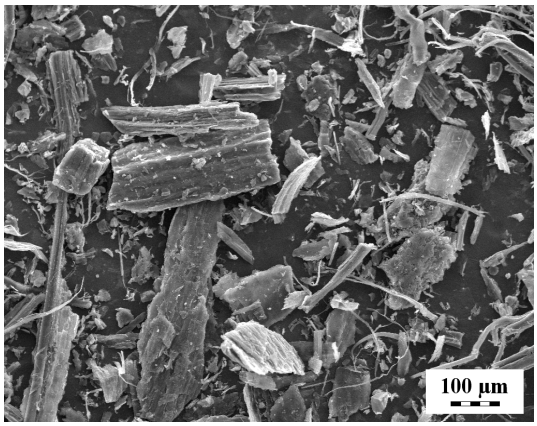


Fig. 4.1.5. Sample of hemp fibres.

4.2 Polymers

4.2.1 Epoxy Resin

As thermoset epoxy resin marketed by Spolek pro chemickou a hutní výrobu a.s., Ústí nad Labem with brand name ChS-Epoxy 371 (data sheet in Tab. 4.2.1) was chosen. The used resin was lightly yellow with density of 1.13 g/cm³. The glass transition temperature was 48 °C.

Tab. 4.2.1
Technical data sheet of ChS-Epoxy 371

Property	Value
Viscosity [Pa s/23 °C]	20–70
Tensile Strength [MPa]	42
Young's Modulus [MPa]	2500
Flexural Strength [MPa]	88

Hardeners are necessary for thermoset in processing. Diethylentriamin with brand name P11, marketed by Spolek pro chemickou a hutní výrobu a.s., Ústí nad Labem too, was used as the hardener in this case, with hardening condition of 25 °C and 48 hours of hardening time.

4.2.2 Polypropylene

Two types of polypropylene were used. One was heterogeneous copolymer polypropylene (block copolymer) with brand name Domolen 2448 L (technical data in Tab 4.2.2) from company DOMO. This PP was a heteroplastic copolymer with PE-units, its densi-

ty was 0.91 g/cm^3 (ISO 1183) and melting point 163 °C (ISO 3146). It was formulated with a nucleation and antistatic stabilisation package.

Tab. 4.2.2
Technical data sheet of polypropylene Domolen 2448 L

Property	Test method	Value
Melt flow rate		
MFR 230/2.16 [g/10 min]	ISO 1133	6
Technical properties		
Tensile modulus of elasticity (v = lmm/min) [MPa]	ISO 527-2	1150
Tensile yield stress (v = 50mm/min) [MPa]	ISO 527-2	24
Tensile yield strain (v = 50mm/min) [%]	ISO 527-2	7
Tensile strain at break (v = 50mm/min) [%]	ISO 527-2	> 50
Charpy impact strength notched + 23 °C [kJ/m^2]	ISO l79/1eA	18
Charpy impact strength notched – 30 °C [kJ/m^2]	ISO l79/1eA	5

Domolen 2448 L was used in composite systems with recycled paper fibres as filler with and without maleic anhydride coupling agent.

Used coupling agent – maleic anhydride grafted on polypropylene was from company DuPont. Brand name is Fusabond P MD353D and it was a chemically modified polypropylene with melting point 136 °C (ISO 3146).

The other one was heterophasic copolymer polypropylene (block copolymer) with brand name BE170MO (technical data in Tab 4.2.3) from company Borealis A/S, characterised by high impact strength combined with high stiffness and good flow properties.

Tab. 4.2.3
Technical data sheet of polypropylene BE170MO

Property	Test method	Value
Melt flow rate		
MFR 230/2.16 [g/10 min]	ISO 1133	13
Technical properties		
Tensile modulus of elasticity (v = l mm/min) [MPa]	ISO 527-2	1250
Tensile yield stress (v = 50 mm/min) [MPa]	ISO 527-2	25
Tensile yield strain (v = 50 mm/min) [%]	ISO 527-2	6
Hardness, Rockwell [R-scale]	ISO 2039-2	86
Charpy impact strength notched + 23 °C [kJ/m^2]	ISO l79/1eA	8
Charpy impact strength notched – 20 °C [kJ/m^2]	ISO l79/1eA	4

This PP had density 0.902 g/cm^3 (ISO 1183) and melting point was 230 – 260 °C (ISO 3146).

BE170MO was used in composite systems with bamboo or hemp fibres as fillers with and without plasma treatment of polymer matrix. Polypropylene was treated by cold plasma with oxygen gas or air.

4.2.3 Polyvinyl Alcohol

Polyvinyl alcohols (types 4-88 – homopolymer and GF 4-86 – copolymer) marketed by Kuraray Specialities Europe with brand name Mowiol were used (data sheet in Tab. 4.2.4). Used Mowiols were flammable white powders, changing to yellow in colour upon heating, with specific gravity 1.25–1.32 [g/cm³] and bulk density 0.4–0.7 g/cm³.

Tab. 4.2.4
Technical data sheet of PVA 4-88 and GF 4-86 [29]

Property	Value
Viscosity* (DIN 53 015) [mPa s]	4.0 ± 0.5
Degree of hydrolysis (saponification) [mol. %]	87.7 ± 1.0
Ester value [mg KOH/g] (DIN 53 401)	140.0 ± 10.0
Residual acetyl content [wt. %]	10.8 ± 0.8
Volatile content [wt./wt. %]	< 5.0
Methanol content [wt./wt. %]	< 3.0
Ash content** [wt./wt. %]	< 0.5
pH	5–7

* of a 4 % aqueous solution at 20 °C
** calculated as Na_20

Mowiol is manufactured from polyvinyl acetate by alcoholysis using a continuous process. The both used types of PVA were partially hydrolysed. Their glass transition temperature is 58 °C and they melt at 150–190 °C. These partially hydrolysed Mowiols dissolve in water much faster than the fully hydrolysed grades. Mowiols are not soluble in animal, plant and grease oils and neither organic solvent. They soften or are soluble in acids and alkalis.

5 Methods

5.1 Preparation of Fibres

The defibrillation treatment was applied on three types of cellulose fibres: Cware F10.2 and fibres from recycled paper PSP-grey (unbleached) and PSP-white (bleached). Before treatment, the fibres were scanned by fibre quality control and characterisation system Fibreshape System by Innovative Sintering Technologies Ltd.

Fibres were treated by several mechanical, chemical and mechano-chemical methods. These methods are summarised in table 5.1.1.

Tab. 5.1.1
Mechanical and chemical treatment of fibres

Method	Cware F10.2	PSP-grey	PSP-white
Referential	x*	x	x
Friction	x	–	–
Milling	x	–	–
Ultrasonic	2 h, 3 h	24 h	24 h, 100 h
NaOH	2 %	10 %	10 %
5 % NH_3 + 95 % H_2O_2	–	–	12 h
Homogeniser	–	30 MPa/10 min	–

*x means used method

Mechanical treatment by friction was made in chemical mortar and pestle and a coffee mill was used for milling.

An ultrasonic cleaner for aqueous cleaning agents (model Sonorex Super Compact Ultrasonic Cleaner, company Bandelin) was used as ultrasonic bath.

Two types of chemical bath were used in ultrasonic device. The first one was the solution of 2 % or 10 % of NaOH in distilled water. The second one was solution of 5 % NH_3 with 95 % H_2O_2. Fibres treated by these chemicals were washing by distilled water sequentially.

The used homogeniser produced by the company APV Schröder, Gaulin LAB 1 DTBS is device which is able to treat 60 l/h with maximal pressure 70 MPa. Homogenisation is a mechanical treatment of the water solutions with small particles and fibres which are brought about by passing solution under high pressure through a tiny orifice, which results in a decrease in the average diameter and an increase in number and surface area, of the particles.

The homogeniser consists of a 3 cylinder positive piston pump. It operates on a similar basis as a car engine and a homogenising valve. The pump is turned by electric motor through connecting rods and crankshaft.

3, 6, 9 and 30 wt. % of defibrillated and nondefibrillated fibres were used to form test pieces. All fibres were dried for 24 hours at a temperature of 105 °C before processing.

5.2 Composite Processing

5.2.1 Casting of Epoxy Resin

Casting method was used to obtain test pieces of composites from epoxy resin with hardener in ratio 100:7 with or without natural cellulose fibres.

Three-pieces-forms made from dural in combination with polymethyl methacrylate with breather holes for evacuation or hardening by pressure above atmospheric (0.7± 0.1) MPa were used. Chemically indifferent solution of beeswax in petrol as thin film was used for separation in this case. Test pieces (70 ± 0.1) mm long with area of cros-section (32 ± 0.6) mm^2 were discarded and deburred.

Polymer and composite test pieces were stored in climate chamber (RUMED 4101) for 16 hours at 23 °C and 48 % humidity according to norm DIN 50 014 before measurements of mechanical properties.

5.2.2 Extrusion of Polypropylene and Polyvinyl Alcohol

The extrusion process was used to prepare granulate of pure polymers (PP and PVA), polymers with coupling agent, cellulose fibres and coupling agent together with natural cellulose fibres.

Every compound was dried at a temperature of 60 °C (polymers) and 105 °C (fibres). Polypropylene and the coupling agent maleic anhydride were dried for 16 hours, polyvinyl alcohol and fibres for 48 hours. The processing parameters of extrusion which were the most suitable ones and were discovered and tested are shown in Figs. 5.2.1. and 5.2.2.

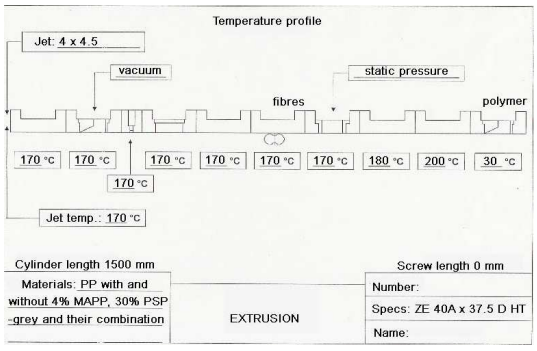


Fig. 5.2.1. Parameters of extrusion of pure PP and PP with additives.

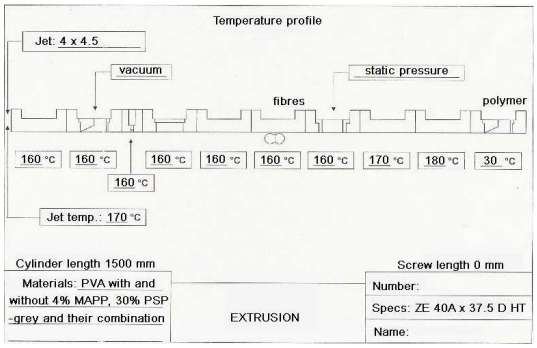


Fig. 5.2.2. Parameters of extrusion of pure PVA and PVA with additives.

In this case, extrusion machine type ZE 40A x 37.5 K HT (company Berstorff) was used. The extrusion unit consists of two screws with diameter 43 mm and length 1 500 mm. The polymers with additives (coupling agent and fillers) were melted and mixed in the extrusion machine after reaching the melting point of polymer matrix. Composite was extruded after mixing with screws and cooled in suitable environment (water or air). Such composite strings go to the cutting machine, where they are granulated with a blade.

5.2.3 Injection Moulding of Polypropylene and Polyvinyl Alcohol

The extruded granulates were used as initial material for the next operation – injection moulding.

Injection moulding machine was used to produce test pieces for tensile and impact tests from the produced composites. Injection moulding process was done by a machine from company Boy type Boy 22S Dipronic.

Each granulate was dried for 24 hours before processing. Dry granulate was put into the injection moulding machine and plasticised. Together with mixing, the granulate was heated up with heating units until it reached the melting point (temperature parameters of injection moulding are in Tab. 5.2.1). After achieving the optimised injection moulding temperature, the polymer or composite was injected into the form of the test piece (type 1B for tensile test according to DIN EN 10002) and it was cooled down for few seconds. Test pieces were cooling on air after being ejected from the form.

This method was used for polymer matrices of polyvinyl alcohols Mowiol 4-88 and GF 4-86 and polypropylene Domolen 2448L with and without MAPP coupling agent.

Similar method of plasticising was used to form test pieces of composites with polypropylene BE170MO matrix with and without plasma treatment. In this case after homogenising and plasticising, composite material was put to a compression mould with the chamber size 150□150□1.8 mm and closed in heated-platen press produced by company Fontjne Holland for 1 min at a temperature of 200 °C and pressing power 100 kN.

Compression mould was cooled in heated-platen press by water to a temperature of 30–40 °C. Test pieces of the type 1BA were milled out of excluded tablet according to the norm ČSN EN ISO 527-2.

Tab. 5.2.1
Temperature parameters of injection moulding adjustable by four Fe-CuNi – thermoelements

Material	Jet temperature [°C]	1. Heating zone [°C]	3. Heating zone [°C] Material area
PVA	190	200	140
PVA + 4 wt. % MAPP	190	200	140
PVA + 30 wt. % PSP-grey	210	210	140
PVA + 30 wt. % PSP-grey + 4 wt. % MAPP	200	210	140
PP + 30 wt. % PSP-grey	170	170	160
PP + 30 wt. % PSP-grey + 4 wt. % MAPP	170	170	160

* 2nd heating zone was not used

5.2.4 Casting of Polyvinyl Alcohol Water Solution

Various methods were used to form composites with natural cellulose fibres embedded in polymer matrices. Test pieces of polyvinyl alcohol were cast from solution of polymer and water (20 g of PVA in 100 ml distilled water) with or without embedded natural cellulose fibres. Two methods of casting were applied.

One method was to cast water solution of polymer or composite to Petri dish (150 20 mm). Test pieces type 2 according to the norm ČSN EN ISO 527-3 were cut up of excluded tablet after drying of cast material on air.

The other method was to cast water solution of polymer or composite material to two-pieces forms made from stainless steel according to norm for test pieces type 1B for tensile test DIN EN 10002.

5.3 Measurement of Mechanical Properties

5.3.1 Tensile Test

Mechanical properties – tensile strength and Young's modulus were measured with tensile test on universal material testing machine with automatic recount produced by company Instron Corporation (Buckinghamshire, England) type 4206.

The tensile test was based on the norm number EN ISO 527-4 at a temperature of (23 ±2) °C and 50 % of relative humidity. Cross-head speed and maximal loading changed with used material of test pieces:

- polyvinyl alcohol matrix – 50 mm/min. and 0.5 kN;

- polyvinyl alcohol matrix and polypropylene matrix – 2 mm/min. and 50.0 kN;
- polypropylene matrix – 20 mm/min. and 0.5 kN;
- epoxy resin matrix – 5 mm/min. and 5.0 kN.

5.3.2 Impact Test

As an additional method to determine mechanical properties, impact test was used. The response of a material to abrupt loading is measured. The most common laboratory test configuration is the pendulum machine. Zwick Pendulum machine 5113 with 7.5 J hammer was used.

Pendulum impact test machines measure the energy absorbed in fracturing the test specimen. The measurement was made according to Charpy, norm DIN EN ISO 179.

Polymer and composite test pieces of the type 1B were prepared for testing according to norm ISO 3167. Test pieces were stored in a freezer to reach testing temperature -30 °C for 16 hours before measurement.

5.3.3 Scanning Electron Microscopy

Fracture surfaces of specimens from test pieces for tensile tests were observed with Scanning electron microscope type JSM 540A produced by JEOL to evaluate distribution of fibres in matrix and adhesion between filler and matrix. Sputter-coating (Sputter Coater Edwards S150B) of the specimens with AuPd was used.

5.4 Measurement of Water Absorption

Water absorption of the used natural cellulose fibres and composite systems with EP, PP and PVA matrices was measured. The amount of moisture absorption was determined by measuring its change in mass – difference between initial mass and mass after expo-sure.

Test pieces with PP and EP matrices were stored at a constant temperature of 23 °C in distilled water for 24 hours. Fibres and test pieces with PVA matrix were stored at a constant temperature of 23 °C and constant 50 % of relative humidity for 24 hours. Samples of cellulose fibres and test pieces of composites were put in drying oven. Temperature of drying oven was (110 ± 5) °C and samples and test pieces were removed at fixed intervals and weighed on laboratory balance KERN EW220-3NM (company Kern and Sohn GmbH). After weighing, they were returned to the oven and the process was repeated until the mass of samples and test pieces was constant. The rate of absorbed water loss was fairly rapid in the early stages of conditioning, it was therefore necessary to

make more frequent mass measurements. The rate was decreasing with time. The ab-

$$M = \frac{\square w_{wet} - w_{dry} \square}{w_{dry}} 100[\ \%]$$

sorbed water content, M, can be determined as:

where the wet and dry mass of samples are denoted by w_{wet} and w_{dry} [79].

6 Results and Discussions

6.1 Mechanical Properties of Composites

Two types of polymer matrices are usually used in composite systems – thermoset and thermoplastic. Three types of polymer matrix were selected for this research work: epoxy resin representing hydrophobic thermoset and two thermoplastic polymers – non-polar polypropylene and polar polyvinyl alcohol.

6.1.1 Epoxy Resin

Epoxy resins are one of the most commonly used matrices in composite systems especially in combination with glass, carbon or aramid fibres. The question is, whether natural cellulose fibres can replace these common fillers.

Based on preliminary experiments, the filling fraction was restricted to 9 % in case of composite systems made from epoxy resin. It was difficult to form test pieces at this stage of filling mainly when flax fibres were used as a filler.

Figure 6.1.1. summarises the results of tensile strength measurements of composites with epoxy resin matrix. The addition of 3–9 wt. % of cellulose fibres results in decrease

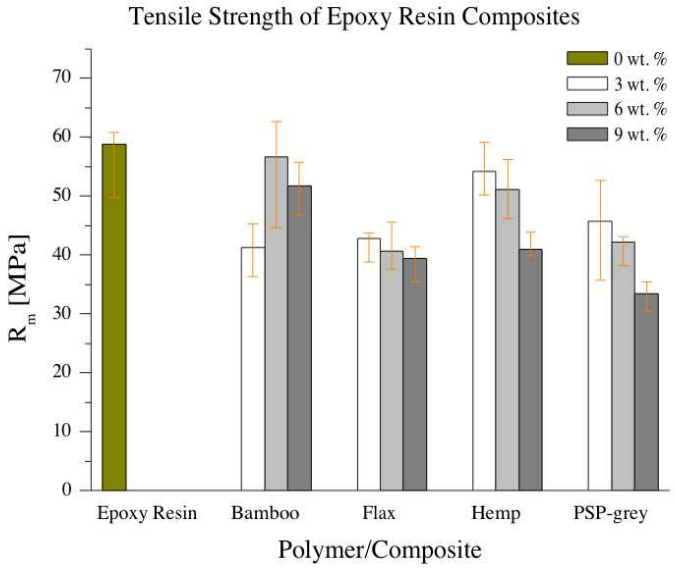


Fig. 6.1.1. Comparison of the tensile strength R_m [MPa] of cast pure epoxy resin and cast composite systems with EP matrix and different cellulose fibres as a filler and its different filling fraction.

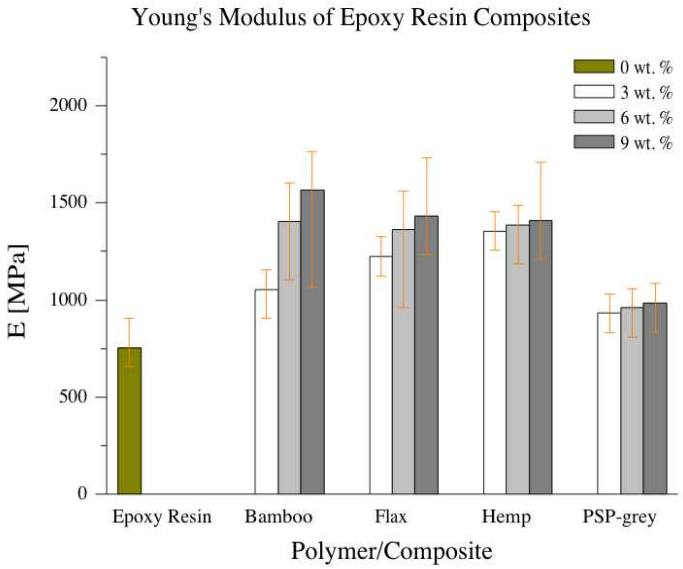


Fig. 6.1.2. Comparison of Young's modulus E [MPa] of cast pure epoxy resin and cast composite systems with EP matrix and different cellulose fibres as a filler and its different content.

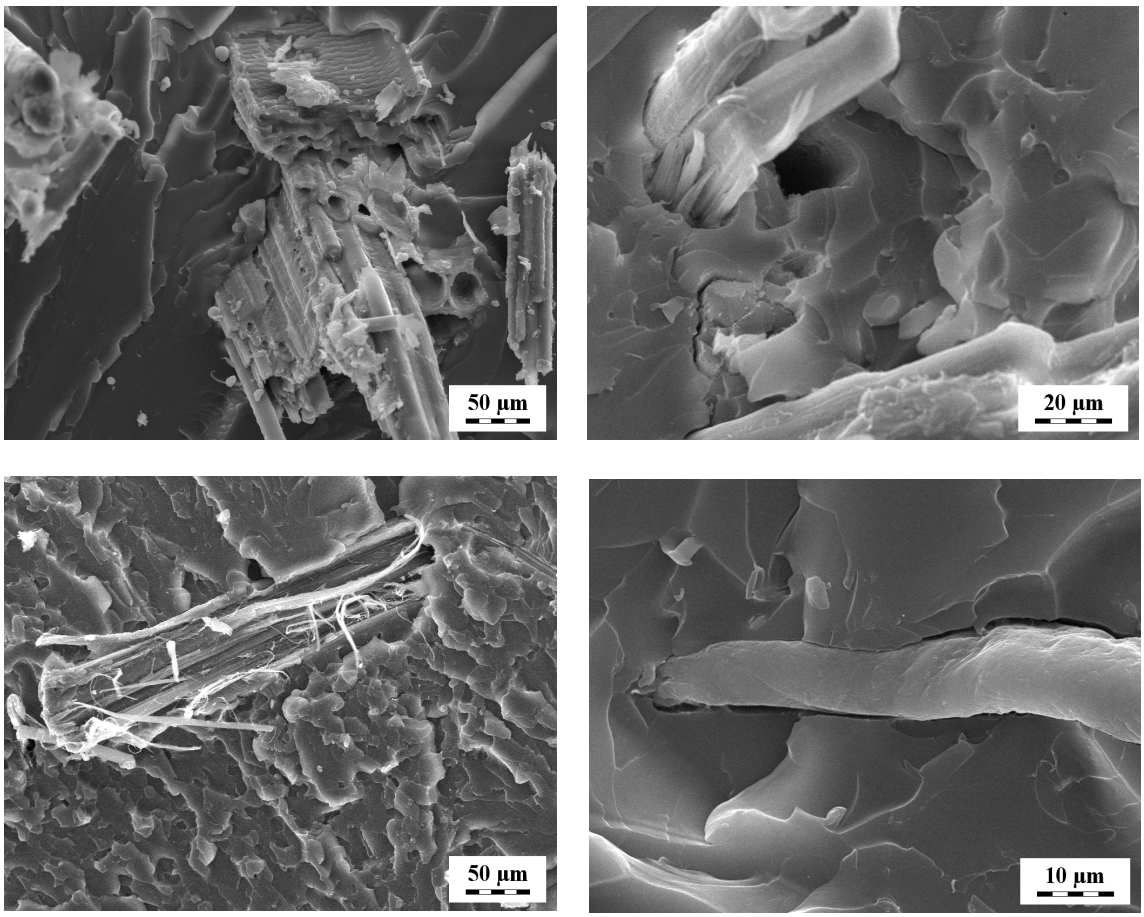
of the tensile strength from 4 % (6 wt. % of bamboo fibres) to 44 % (9 wt. % of PSP-grey recycled fibres) in comparison with pure EP matrix (59 MPa).

The measured Young's modulus of the epoxy resin composites is in figure 6.1.2. Composites with filler from bamboo fibres had the best results of the Young's modulus – two times higher modulus than that of pure EP (750 MPa). These composites also evidenced the highest dependence on filling fraction value embodied bamboo fibres. The other investigated fibres (hemp fibres and PSP fibres from recycled paper) showed much less pronounced dependence on filling fraction, but also these fillers resulted in enhancement of the Young's modulus with respect to the pure epoxy resin. The modulus increased from 24 % for 3 wt. % of PSP-grey recycled fibres up to 109 % for 9 wt. % of bamboo fibres. (Tables of measured values are in Appendix A in Tab. A.1 – Tab. A.2.)

SEM picture Fig. 6.1.3. of fracture surfaces of composite specimens showed poor adhesion between fibres and matrix except for hemp fibres. Gaps between fibres and EP were found and dispersion of fibres was not homogeneous. Few fibres could be seen, pulled out of the matrix during tensile measurement.

Basic theory of composite materials predicted increased values of tensile strength and Young's modulus after embedding of reinforcing fibres to a matrix [81]. Raising values of Young's modulus measured in case of raising volume of natural cellulose fibre reinforcement in epoxy resin matrix correspond to this theory, whereas the trend of obtained values of the tensile strength was just opposite.

The addition of 3–9 wt. % of cellulose fibres decreased the tensile strength by 4 % (6 wt. % of bamboo fibres) to 44 % (9 wt. % of PSP-grey recycled fibres) in comparison



C) **D)**

Fig. 6.1.3. Fracture surface of epoxy resin composites.

A) Fracture surface of EP matrix with 9 wt. % of bamboo fibres.

B) Micrograph of specimen fracture surface of EP matrix with 3 wt. % of flax fibres shows low fibre – matrix adhesion and long voids on borders of fibres with matrix.

C) Fracture surface of EP matrix with 3 wt. % of hemp fibres – good matrix-fibre adhesion can be seen from micrograph.

D) Micrograph of specimen fracture surface shows almost no adhesion and large and long voids between EP matrix and 3 wt. % of PSP-grey fibres as filler.

with pure EP matrix. This phenomenon could be explained by imperfect adhesion between hydrophilic fibres and hydrophobic matrix and occurrence of high amount of cavities, as can be seen from the SEM pictures of the fracture surfaces. Content of cavities in composite systems has been reported to affect significantly mechanical properties of the composite material [80]. Cavities cause a decrease of efficient supporting cross-section transferring load and they perform as a stress raiser leading to reduction of tensile strength [81, 82].

The increase in the Young's modulus of filled EP was given by presence of strengthening fibres, that bear part of the tension and they imparted stiffness to the reinforcing materi-al. According to that theory, raising values of Young's modulus were measured in case of raising volume of natural cellulose fibre reinforcement in epoxy

resin matrix especially by the composites with filler out of bamboo fibres. These composites reached absolutely the highest values respectively in dependence on filling fraction. Young's modulus was two times higher than pure EP in this case. The rest of the used filler did not have so ex-pressive influence on modulus of resulting composite systems. Generally modulus in-creased by from 24 % (3 wt. % of PSP-grey recycled fibres) to 109 % (9 wt. % of bam-boo fibres).
Poor adhesion between fibres and matrix except bamboo and hemp fibres is evident from micrographs (Fig. 6.1.3.) of these composite systems fracture surfaces. Additionally, the dispersion of fibres was not homogeneous and gaps between fibres and EP matrix were found. Few fibres were pulled out from the matrix during the tensile measurement. Inhomogeneities evident from micrographs are due to the technique of their preparation – casting of highly viscous composite system with EP matrix and cellulose fibres. Inho-mogeneity of test pieces was explanation of decrease in tensile strength. Pressure form-ing in vacuum is more suitable processing method as it inhibits formation of cavities. Unfortunately, this method was not available in our laboratory.

6.1.2 Polypropylene

The present-day trend is the application of thermoplastic with natural cellulose fibres in composites, both in the research and in the industry [83]. A lot of studies deals with adhesion, and it is very common to use maleic anhydride acid as coupling agent. But it could be possible to use polymer matrices treated by plasma.

6.1.2.1 Polypropylene with Maleic Anhydride Grafted Polypropylene

Polypropylene Domolen 2448 L (Fig. 6.1.5. A) was used as a matrix for composites with natural cellulose fibres. To increase the adhesion between fibres and hydrophobic polymer, the maleic anhydride tends to be used as a coupling agent for grafting the polypropylene surface. Composite test pieces were prepared from the pure and grafted polypropylene both filled with PSP-grey recycled cellulose fibres.

Results of tensile strength and Young’s modulus measurements are summarised in figure 6.1.4. In comparison with pure polypropylene and polypropylene with 4 wt. % of MAPP as matrices, after embedding 30 wt. % of PSP-grey recycled cellulose fibres, ten-sile strength increased, and Young’s modulus as well. Tensile strength increased by 50 % after incorporating dry PSP-grey fibres to the PP with coupling agent as matrix. Good results of Young’s modulus were reached by use of pure PP matrix with 30 wt. % of PSP-grey. The Young’s modulus increased by 260 %. In case of polypropylene matrix with MAPP, the Young’s modulus increased by 50 % after incorporating PSP-grey fibres.

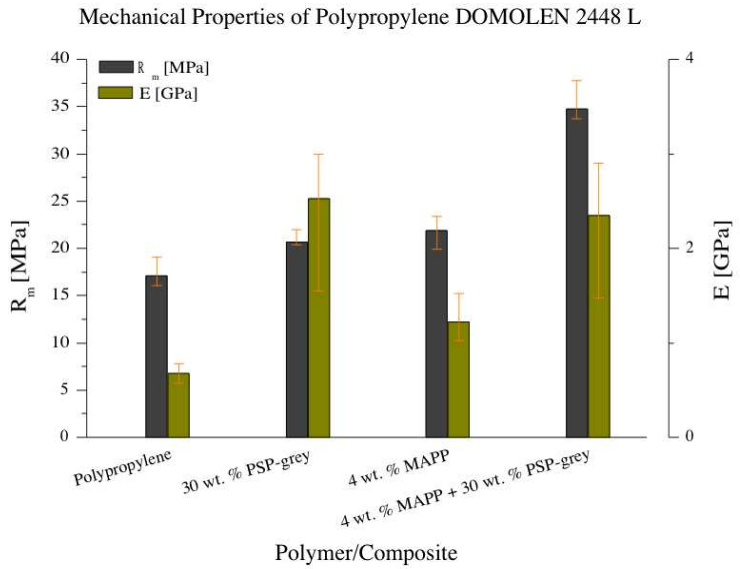
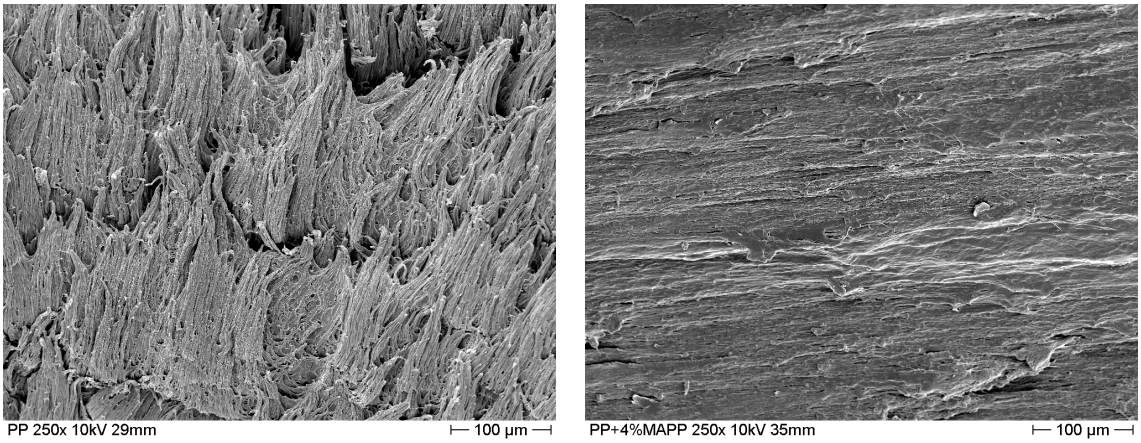


Fig. 6.1.4. Mechanical properties (tensile strength R_m [MPa], Young's modulus E [MPa]) of moulded pure polypropylene Domolen 2448 L and composite systems with 30 wt. % of PSP-grey recycled cellulose fibres or 4 wt. % of MAPP and their combination.

Compared to the previous mentioned results, Young's modulus and tensile strength increased evidently according to the theory after cellulose fibres were embedded. The application of maleic anhydride coupling agent markedly improved this trend. (Table of measured values is in an Appendix B in Tab. B.1.)

Interaction between fibres and polypropylene matrix with and without addition of MAPP as coupling agent is evident from next pictures – Figs. 6.1.5. and 6.1.6. Improvement of adhesion that participates on improvement of mechanical properties is evident



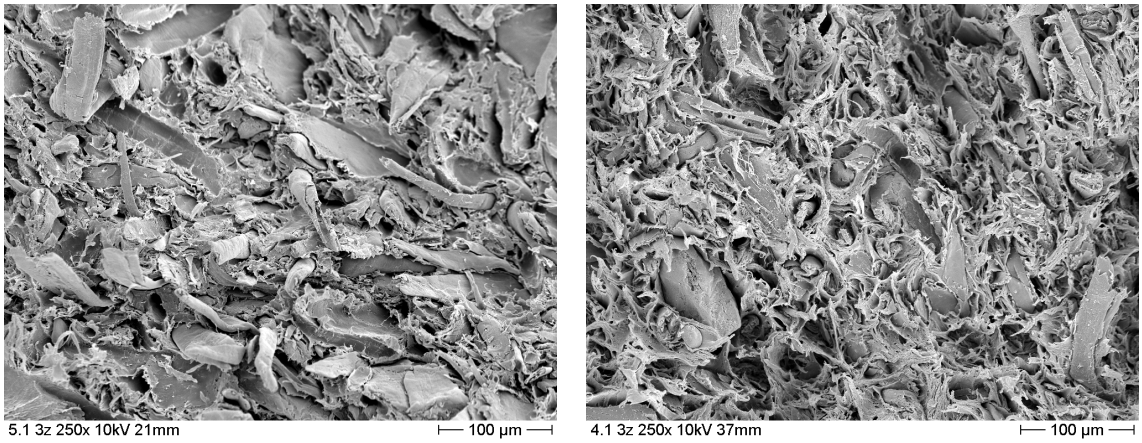
A) **B)**

Fig. 6.1.5. Fracture surface of polypropylene Domolen 2448 L.

A) The micrograph shows fracture surface of PP specimen processed by injection moulding. This fracture is plastic and it shows typical behaviour of polypropylene.

B) Plastic fracture surface of polypropylene Domolen 2448 L with 4 wt. % of maleic anhydride grafted polypropylene (MAPP) processed by injection moulding.

from these pictures. Maleic anhydride grafted polypropylene changes properties of pure polymer matrix and it behaves as plasticiser in connection with polypropylene.



A) **B)**

Fig. 6.1.6. Fracture surface of polypropylene with 30 wt. % of PSP-grey recycled cellulose fibres.

A) The micrograph shows fracture surface of composite specimen processed from polypropylene as a matrix with PSP fibres. The fracture surface area shows ductile behaviour with typically pulled-out fibres that refer to not really good adhesion.

B) Fracture surface of PP with 4 wt. % of MAPP and 30 wt. % of PSP-grey fibres also shows ductile behaviour. The coupling agent has improved adhesion between matrix and fibres, which is evident from the picture.

Mechanical properties of polypropylene composites changed according to the theory [80–82] – tensile strength (by 50 %) and Young's modulus (practically about by 260 %) increased after embedding 30 wt. % of PSP-grey recycled fibres to matrices from PP with and without 4 wt. % of MAPP as coupling agent. The lower increase of modulus measured by composites with added MAPP can be explained by acting of the coupling agent in connection with PP matrix as a plasticiser. All test pieces could be considered as anisotropic due to the processing by injection moulding.

Micrographs showed the difference between both materials with and without coupling agent (pure matrices Fig. 6.1.5. or composites Fig. 6.1.6.). Composite processed from polypropylene matrix with PSP fibres with 4 wt. % of coupling agent MAPP showed ductile behaviour and the coupling agent improved adhesion between matrix and fibres as it can be seen from micrographs of fracture surface of composite with polypropylene as a matrix and PSP fibres. This fracture surface area showed ductile behaviour but with typically pulled-out fibres which indicate poor adhesion between the matrix and the fibres (Fig. 6.1.6.). Almost no cavities occurred in these test pieces. It is a sign of the suitable processing method application.

6.1.2.2 Polypropylene with Plasma Treatment

Only bamboo and hemp fibres were used for this study because of easier processibility to the polymer matrix due to their fibrous structure.

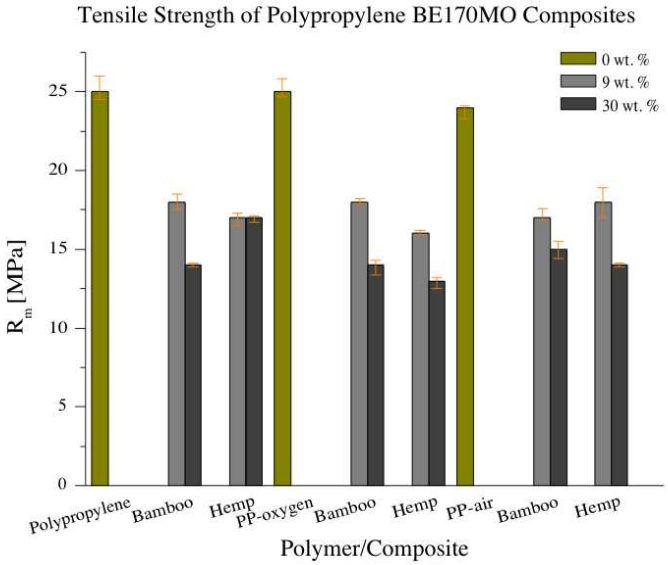
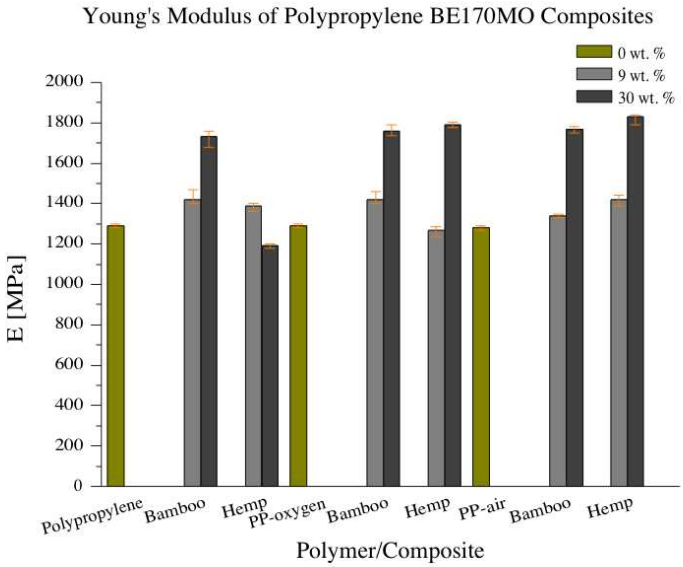


Fig. 6.1.7. The tensile strength [MPa] of pure polypropylene and composite systems with PP matrix and different cellulose fibres as a filler and its different filling fraction (one group of composites with PP matrix was treated by oxygen plasma, the second by air plasma).

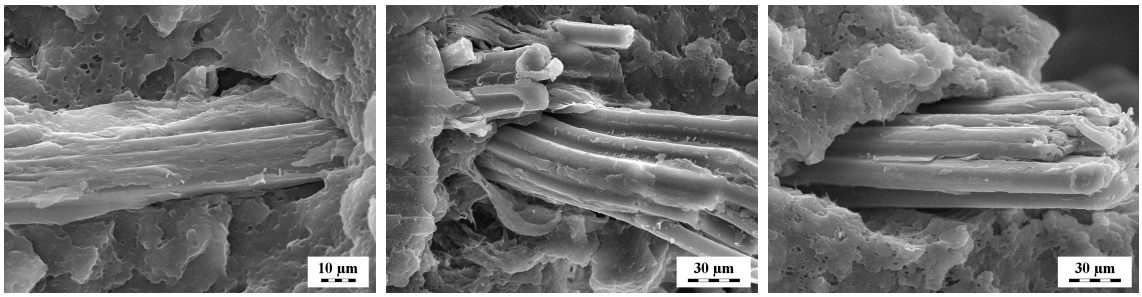
Fig. 6.1.8. Young's modulus [MPa] of pure polypropylene and composite systems with PP matrix



and different cellulose fibres as a filler and its different content (one group of composites with PP matrix was treated by oxygen plasma, the second by air plasma).

Tensile strength (Fig. 6.1.7.) decreased, in comparison with pure polypropylene matrices, after embedding 9 or 30 wt. % of bamboo or hemp fibres to the pure polypropylene BE170MO matrix and to the polypropylene matrices treated either by oxygen or air plasma. In case of plasma treated polypropylene, the increase of adhesion was expected but it did not happen. A lot of inhomogeneities and voids were in all produced composites and no evident adhesion of treated polymers to natural cellulose fibres can be seen from all micrographs Figs. 6.1.9. and 6.1.10.

Young's modulus (Fig. 6.1.8.) increased after embedding fibres and it grew with the amount of used fibres. Maximal increase of Young's modulus was 30 % after incorporating 30 wt. % of fibres. (Table of measured values are in Appendix B in Tab. B.2 – Tab. B.3.)



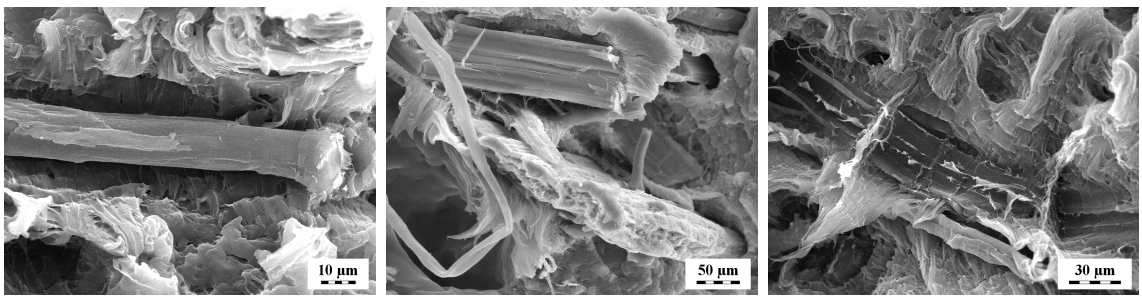
A) **B)** **C)**

Fig. 6.1.9. Fracture surface of heterophasic copolymer polypropylene BE170MO with 9 wt. % of bamboo fibres.

A) Micrograph of fracture surface of composite specimen shows low adhesion between untreated polypropylene matrix and bamboo fibres.

B) Micrograph of fracture surface of composite specimen shows pure adhesion between PP matrix treated by oxygen plasma and bamboo fibres.

C) Micrograph of fracture surface of composite specimen shows low adhesion between heterophasic copolymer PP matrix treated by air plasma and bamboo fibres.



A) **B)** **C)**

Fig. 6.1.10. Fracture surface of polypropylene BE170MO with 9 wt. % of hemp fibres.

A) Almost no adhesion between untreated PP matrix and hemp fibres can be seen from micrograph.

B) Micrograph of fracture surface of composite specimen shows pure adhesion between PP matrix treated by oxygen plasma and hemp fibres.

C) Micrograph of fracture surface of composite specimen shows imprint of bundles of hemp fibres and low adhesion between them and PP matrix treated by air plasma.

Bamboo and hemp fibres were used as a filler in the composite systems with matrix made from polypropylene treated by air and/or oxygen plasma. Mechanical properties changed due to embedding of mentioned natural cellulose fibres but the tensile strength even decreased by 30–48 %, in comparison with pure polypropylene matrices, after embedding cellulose fibres. It could be due to incompatible connection of hydrophobic or hydrophilised polymer matrices and hydrophilic cellulose fibres. Resulting composites had highly inhomogeneous structure – places with partial or no adhesion and with inhomogeneous morphology of fibres too. Inhomogeneities in structure could happen due to the used processing method. The polymer displays other melting properties which was found during melting experiments. These different properties could happened due to possible cross-linking of particles surface layer in consequence of its interaction with plasma respectively with plasma radiation [84].

Test pieces could be also considered as anisotropic due to the processing by compression moulding that leads to a large variability of the measured values. Ends of fibres considerably influence the decrease in tensile strength of composites reinforced by short fibres. Stress concentrations happen at the ends of the fibres and cause their separation from matrix by microcracks even at low load. It is known from literature that shear stress along fibres between surfaces could separate out fibres from matrix and these emergent cracks begin extent. If it happens by all fibres, fibres would become ineffective and composite material would behave like a bundle of fibres without matrix [80–82]. Demonstration or elimination of this effect requires additional study what is beyond the scope of the presented work. Cavities and voids that are always present in composite systems appeared as another effect. These cavities and voids did not cause only decrease of efficient supporting cross-section of test pieces but they took effect as stress raiser which led to decrease of tensile strength [81].

Young's modulus increased after embedding fibres and it increased with filler content by almost all types of these polypropylene composite systems except one – 30 wt. % of hemp fibres embedded in pure PP matrix. Young's modulus decreased by 7 %. Maximal increase of Young's modulus was 30 % after incorporating 30 wt. % of fibres.

In case of plasma treated polypropylene, the increase of adhesion was expected but it did not happen. A lot of inhomogeneities and voids were in all produced composites and no evident adhesion of plasma treated polymers to natural cellulose fibres could be seen from micrographs (Figs. 6.1.5.–6.1.6.). Influence of plasma treatment, air and oxygen, was rather negative. In spite of the fact that adhesion of plasma treated polymers to metals was good as it was shown in [85], for organic fibres sufficient adhesion was not reached. It is obvious that affection of polymer particles surface layer in consequence of its interaction with plasma respectively with plasma radiation happened and this problem should be studied further.

6.1.3 Polyvinyl Alcohol

6.1.3.1 Injection Moulded Polyvinyl Alcohol

Two types of polyvinyl alcohol were used. The first type PVA GF 4-86 was used at the beginning of the investigation. Small amount of the polymer, deficient for extrusion and

injection moulding process, was mainly used for casting. The second polyvinyl alcohol 4-88 (Fig. 6.1.12. A) had similar properties as far as the solubility was concerned but the mechanical properties were different.

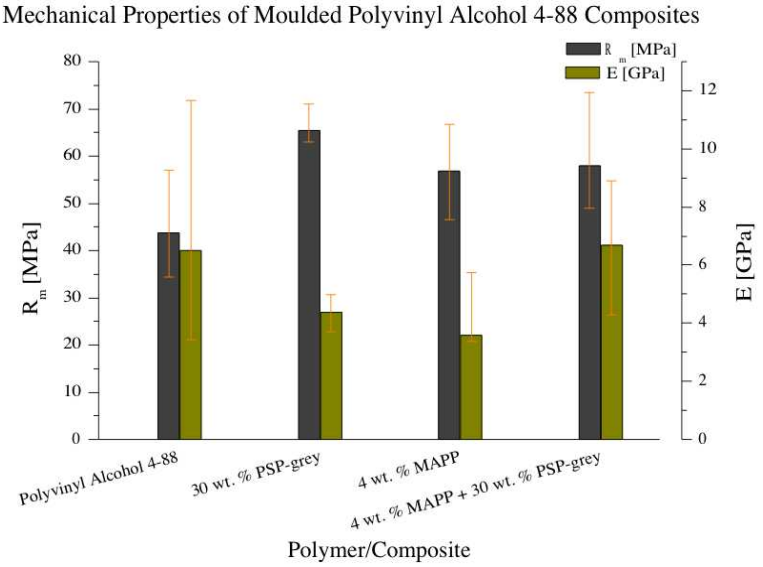


Fig. 6.1.11. Mechanical properties (tensile strength Rm [MPa], Young's modulus E [MPa]) of moulded pure polyvinyl alcohol 4-88 and composite systems with 30 wt. % of PSP-grey recycled cellulose fibres or 4 wt. % of MAPP and their combination.

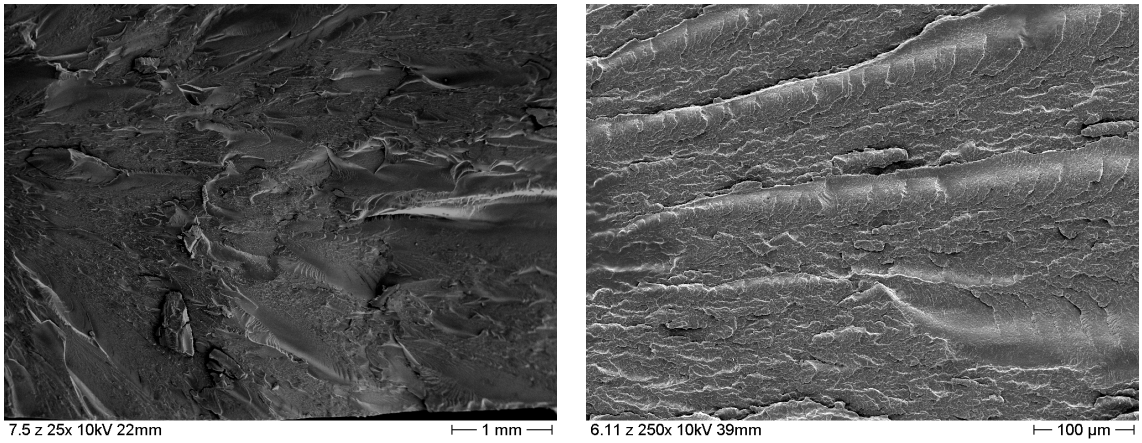
Figure 6.1.11. summarises the results of tensile strength and Young's modulus of moulded composites with polyvinyl alcohol matrix. The test pieces made from PVA 4-88 with 30 wt. % PSP-grey produced by injection moulding showed high tensile strength. The tensile strength increased by 50 % after incorporating of dry fibres to the PVA 4-88 matrix. The PVA 4-88 with MAPP coupling agent had higher tensile strength in comparison with pure PVA 4-88 but after embedding the PSP-grey recycled fibres did not result in any increase in their tensile strength.

Increase of Young's modulus by 85 % was recorded in case of PVA with 4 wt. % MAPP matrix composite after incorporating dry PSP-grey fibres. Composite systems with ma-trix from pure PVA did not increase their modulus after embedding fibres. (Table of measured values is in an Appendix C in Tab. C.1.)

Illustration of fracture surfaces of pure PVA and composites with polyvinyl alcohol or PVA with MAPP matrices and 30 wt. % of PSP fibres are in the following SEMs. Surprisingly it is evident, that addition of coupling agent to the composite system did not change adhesion between fibres and matrix.

Test pieces of PVA were fabricated by extrusion and injection moulding. These processing methods are not recommended and even described by the producer of PVA as impossible, but our test pieces produced by these technologies were satisfactory. The injection moulding of PVA was accomplished due to the possibility to compare the test

pieces made from PVA with other test pieces of composite systems produced by the same technology.

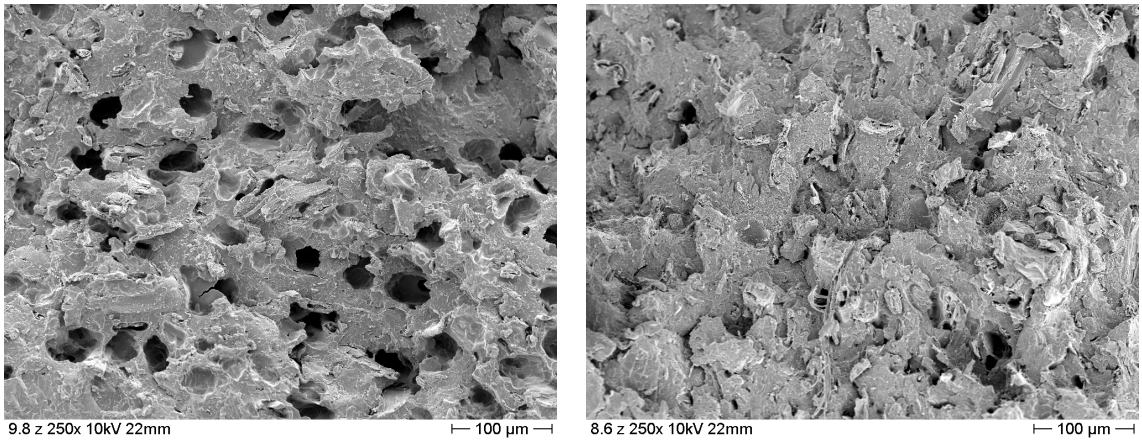


A) **B)**

Fig. 6.1.12. Fracture surface of polyvinyl alcohol 4-88.

A) The micrograph shows fracture surface of specimen of PVA processed by injection moulding. This fracture is brittle like the PVA GF 4-86.

B) Fracture surface of PVA 4-88 with 4 wt. % MAPP processed by injection moulding.



A) **B)**

Fig. 6.1.13. Fracture surface of polyvinyl alcohol 4-88 composites.

A) Fracture surface of PVA 4-88 with 30 wt. % PSP-grey recycled cellulose fibres. Micrograph of fracture surface of inhomogeneous composite specimen shows large amount of cavities.

B) Fracture surface of PVA 4-88 with 30 wt. % PSP-grey fibres and 4 % MAPP. Partially inhomoge-neous fractures surface shows good adhesion between fibres and matrix with coupling agent.

In comparison with pure polyvinyl alcohol, the strength increased according to the theory of used reinforcing fibres in composite materials [80–82]. PVA 4-88 with 30 wt. % PSP-grey showed high tensile strength that increased by 50 % after incorporating dry fibres to the PVA matrix. This happened due to good interaction between the both compo-nents because of cellulose chains react well with -OH groups in PVA chains.

PVA with MAPP coupling agent had higher tensile strength (of about 30 % more) in comparison with pure PVA 4-88 but after embedding fibres the tensile strength did not increase. Dif-ferent strength of PVA 4-88 and PVA + 4 % MAPP could be explained by using of cou-pling agent that behaved as plasticiser [40].

The Young's modulus decreased after embedding 30 wt. % of PSP-grey fibres to the PVA matrix. It could be explained by inhomogeneous structure and large amount of voids furthermore due to fast water absorption of polymer from air humidity during injection moulding process and due to the fact that the plasticiser was not present. In case of PVA with 4 wt. % of MAPP, Young's modulus increased by 85 % after embedding 30 wt. % of PSP-grey fibres. It corresponds with theory for calculation of mechanical properties of composite materials [80–82]. PVA 4-88 without coupling agent had higher Young's modulus if compared PVA 4-88 with MAPP because the coupling agent behaved again as plasticiser in connection with PVA matrix. The polypropylene parts of coupling agent in connection with matrix and fibres behaved as a joint and helped linked chains to move.

As expected additional hydrophilization of hydrophilic polymer matrix did not cause next changes in adhesion between polymer and cellulose fibres.

6.1.3.2 Cast Polyvinyl Alcohol

Natural cellulose fibres are suitable filler to hydrophilic polymer matrices such as polyvinyl alcohol, which is a polymer soluble in water. Embedded cellulose fibres changed their mechanical properties. The Young's modulus markedly increased (in order of hundreds per-cent) in comparison with the pure cast polyvinyl alcohol but, surprisingly, no enhancement of the tensile strength was observed.

The tensile strength is in Fig. 6.1.14. Pure PVA GF 4-86 dissolved in water had strength equal to 11.4 MPa. Tensile strength decreased after cellulose fibres were embedded into the PVA matrix. Cavities (Fig. 6.1.16.) and undissolved particles of PVA (Fig. 6.1.17.) occurred in all test pieces and their number increased with increasing filler content. The best result was obtained for 9 wt. % of filling independent on the type of cellulose fibres. Hemp fibres and PSP-grey recycled fibres showed the best results in all experiments. The only hemp fibres increased the tensile strength by 1.3 %. (Table of measured values in an Appendix C in Tab. C.2)

The increase in Young's modulus which is shown in figure 6.1.15., in case of filled PVA, is due to the presence of strengthening cellulose fibres. Modulus of pure PVA cast from water solution was 65 MPa. It increased after embedding the cellulose fibres to the PVA matrix by 600 % in case of 30 wt. % of hemp fibres. This was the best result; flax, bamboo and PSP-grey fibres increased resulting modulus by 340–440 % (30 wt. % of filling). Only flax fibres did not prove growing tendency of modulus with growing fill-ing fraction. (Table of measured values in Appendix C in Tab. C.3).

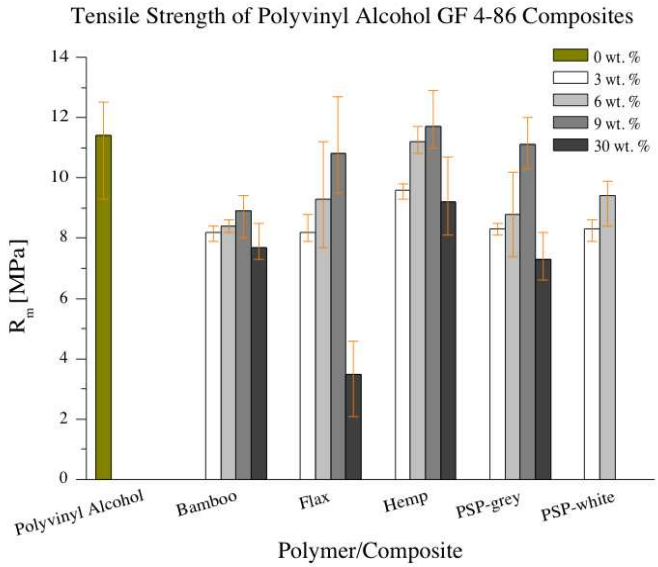


Fig. 6.1.14. Comparison of the tensile strength R_m [MPa] of cast pure polyvinyl alcohol and cast composite systems with PVA matrix and different cellulose fibres as a filler and its different filler fraction.

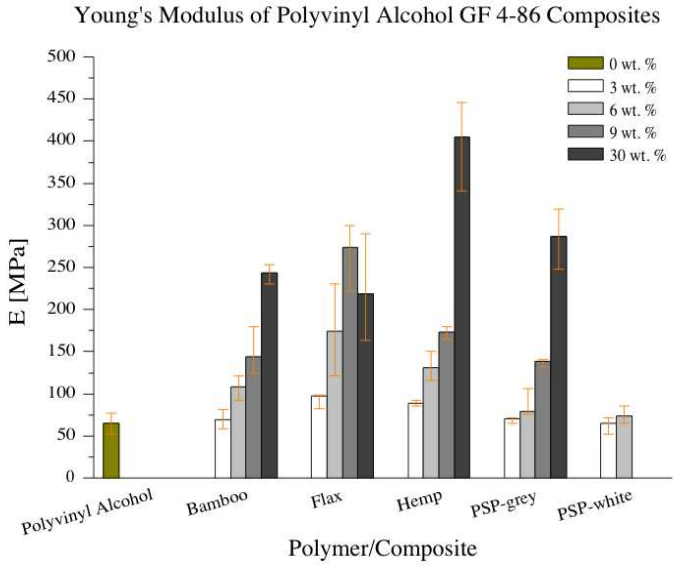


Fig. 6.1.15. Young's modulus E [MPa] of cast pure polyvinyl alcohol and cast composite systems with various content of cellulose fibres.

Following five micrographs show an overview of fracture surfaces of cast composite test pieces with PVA GF 4-86 as a matrix and cellulose natural fibres as a filler (bamboo, flax, hemp, PSP-grey and PSP-white).

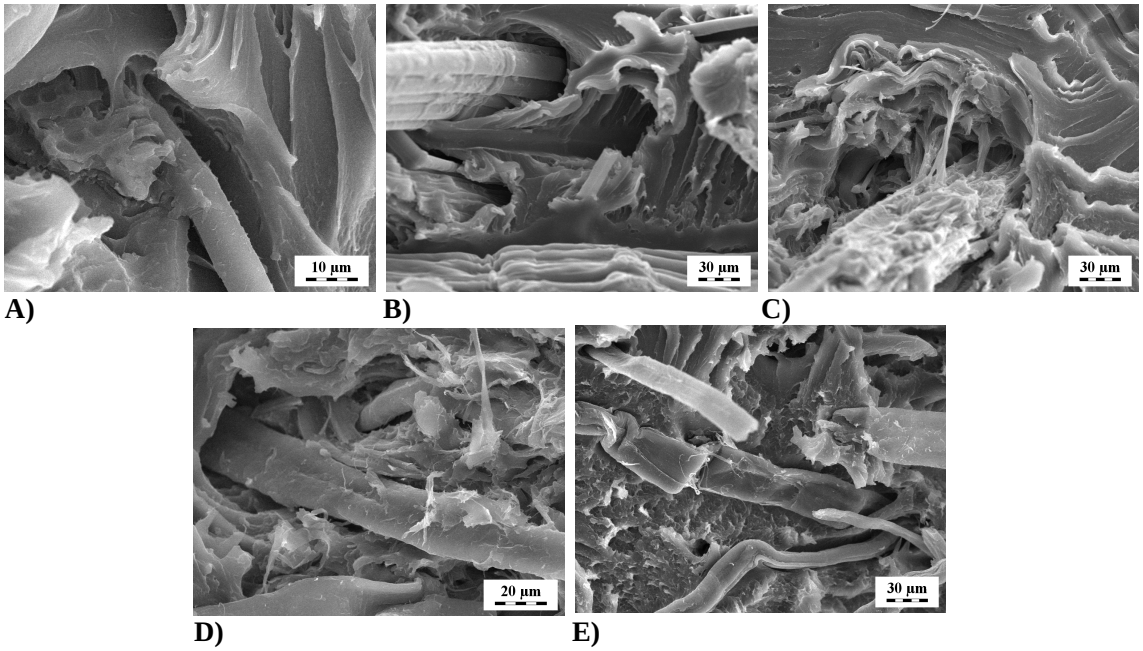
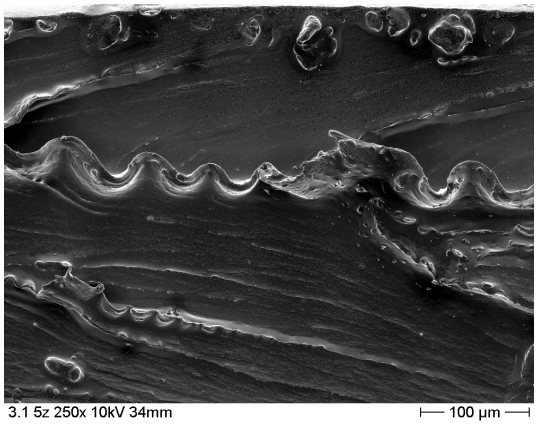


Fig. 6.1.16. Fracture surfaces of cast PVA GF 4-86 as matrix with various types of fibres.
A) 9 wt. % of bamboo fibres – partial adhesion can be seen in places of impurities (rests of middle lamella).
B) 3 wt. % of flax fibres – partial adhesion can be seen on bundles of fibres.
C) 3 wt. % of hemp fibres – fibres are covered by PVA matrix – proof of good adhesion.
D) 3 wt. % of PSP-grey fibres – partial adhesion between mixture of different recycled fibres and PVA matrix can be seen from the micrograph.
E) 3 wt. % of PSP-white fibres – low adhesion between mixture of different bleached recycled fibres



and PVA matrix can be seen from the micrograph.

Fig. 6.1.17. Fracture surface of cast polyvinyl alcohol GF 4-86.
Particles of undissolved PVA granules are seen in the upper part of the micrograph. These specimens were not homogeneous as it can be seen from the micrograph.

Mechanical properties changed after embedding of the above mentioned natural cellulose fibres. Tensile strength of composite systems, against all expectation, did not increase almost in all cases. According to the theory [80], low filling fraction (3 wt. %) decreased tensile strength, which then increased at 9 wt. % of filling and subsequently declined with 30 wt. % of embedded fibres. By increasing the degree of filling, amount of cavities and voids increased resulting in decrease of efficient supporting cross-section of test pieces [81]. Hemp fibres and PSP-grey recycled fibres showed the best results. In case of hemp fibres the tensile strength increased up to 1.3 %.

Young's modulus markedly increased (in order of hundreds of per-cent) in comparison with the pure polymer. Modulus of pure PVA was 65 MPa. Maximal increase (by 600 %) was reached after embedding of 30 wt. % of hemp cellulose fibres to the PVA matrix. Flax, bamboo and PSP-grey fibres resulted in modulus enhancement by 340–440 % when the same filling fraction as for composite system with hemp was used. Young's modulus increase of filled PVA GF 4-86 was caused by presence of strengthening fibres that bear part of the tension. The interaction between the hydrophilic filler and the wa-tersoluble polymer matrix – polyvinyl alcohol happened due to hydrogen bonds.

Fibres were covered by the matrix can be seen from micrographs (Fig. 6.1.16.), it adverts to good adhesion between strengthening fibres and polymer matrix. PSP-white recycled fibres are the exception, because the adhesion was low. This can be explained by chemical pretreatment that bleaches fibres and it changed surface property of cellulose. Considerable inhomogeneities evident from micrographs could be explained by the technique of their preparation – casting of polymer from water solution. Inhomogeneity of test pieces explains the tensile strength decrease. Large amount of cavities decreased efficient supporting cross-section of test pieces [80]. Not only adhesion influences mechanical properties but also cavities that failed to remove. The method of cavities elimination in processing opens new problems to solve.

PSP-grey fibres seem to be a very interesting filler because of their possible re-use as a filler in biodegradable composite systems.

6.2 Defibrillation of Natural Cellulose Fibres

Cellulose microfibres were extracted from a biomass by mechanical and chemical treatment, used methods are summarised in table 5.1.1 (chapter 5 Methods, subchapter 5.1 Preparation of Fibres).

Tab. 6.2.1
Result parameters of Cware F10.2 fibres from Fibreshape System

Average Values	
Counted fibres	1886.0000
Fibre thickness [µm]	17.4000
Fibre length [µm]	161.5000
Aspect ratio [-]	0.2290

Cware F10.2 cellulose fibres and fibres from recycled paper PSP-grey (unbleached) and PSP-white (bleached) were used for defibrillation. Only fibres with length between 5 µm and 150 µm were taken into an account by reason of measuring possibilities of Fibreshape System device. Results of some parameters (amount of counted fibres, size and length of fibres and aspect ratio) of Cware F10.2 and PSP fibres are in Tab. 6.2.1 and Tab. 6.2.2.

Tab. 6.2.2
Result parameters of PSP-grey fibres from Fibreshape System

	Average Values
Counted fibres	108.0000
Fibre thickness [µm]	18.9300
Fibre length [µm]	251.4000
Aspect ratio [-]	0.0038

The volume fraction of fibres length [%] was characterised in dependence on thickness and in dependence on length. The cellulose Cware F10.2 fibres were more homogeneous than PSP fibres. Over 16 % of Cware F10.2 fibres were about 20 µm thick and about 200 µm long (graphs in Fig. 6.2.1. and micrograph Fig. 6.2.3. A). PSP fibres were formed by an inhomogeneous mixture of recycled fibres from paper. Considerable amount – of about 20 % of fibres – had thickness 250 µm and about 16 % 150 µm. Majority of PSP fibres was about 250 µm in length. These results are in Fig. 6.2.2.

There were two steps of the mechanical treatment. At first the fibres were disintegrated in a chemical mortar and pestle. Milling in a coffee mill, tested as the second step in the first experiments, did not contribute to further fibres defibrillation, but only reduced the fibres length as shown in 6.2.3. B. Much better results were obtained by using treatment in ultrasonic bath combined with additional chemical treatment as the second step for defibrillation.

PSP fibres (Fig. 6.2.4. A) treated chemically by 5 % NH_3 + 95 % H_2O_2 were only bleached and no defibrillation was observed (Fig. 6.2.4. B). As the best chemical, the

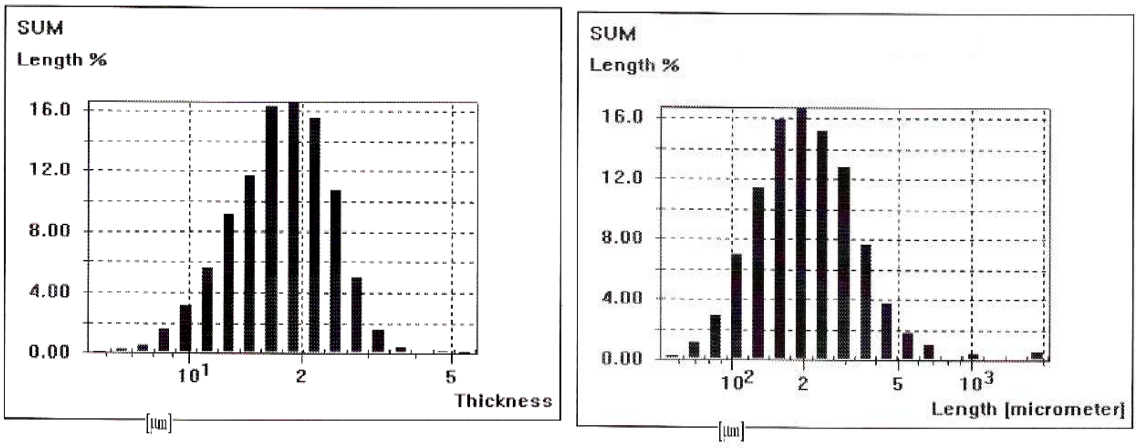


Fig. 6.2.1. Volume fraction of cellulose Cware F10.2 fibres length [%] in dependence on thickness [µm] and length [µm].

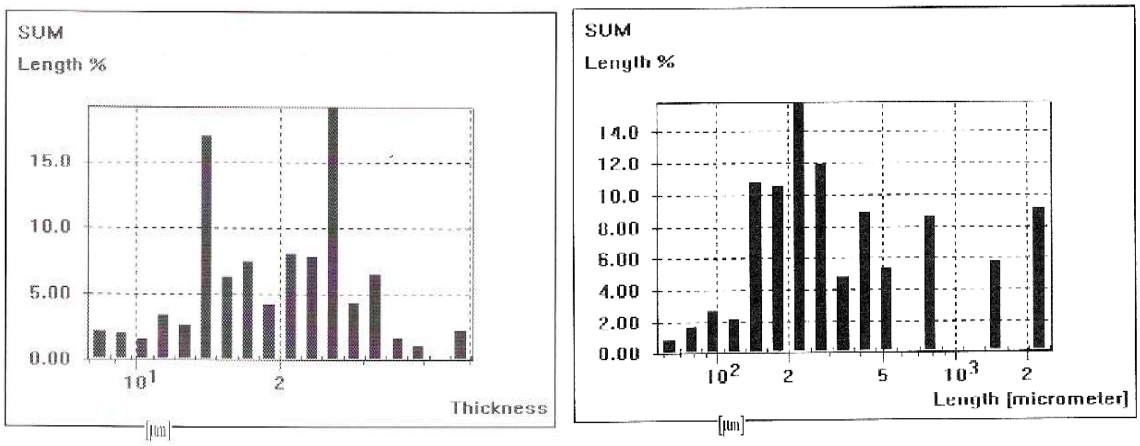
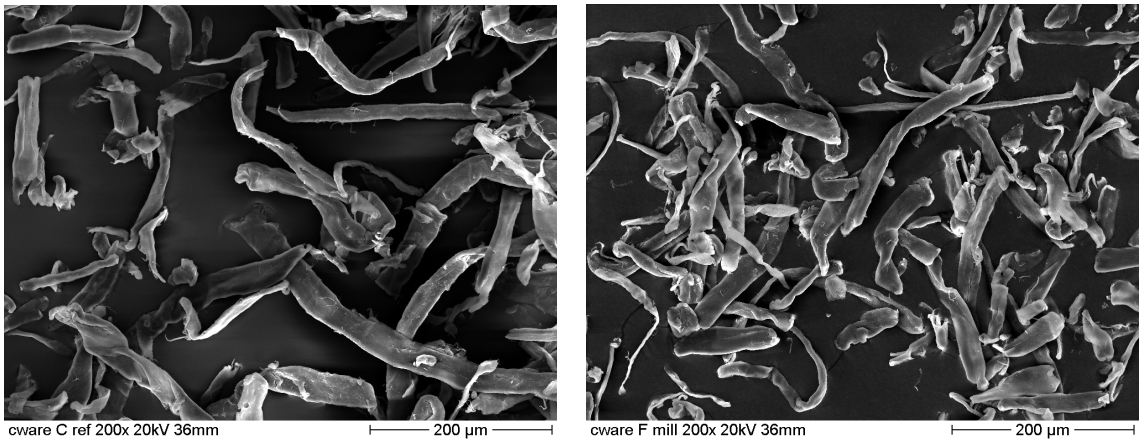


Fig. 6.2.2. Volume fraction of recycled PSP-grey fibres length [%] in dependence on thickness [µm] and length [µm].



A) **B)**

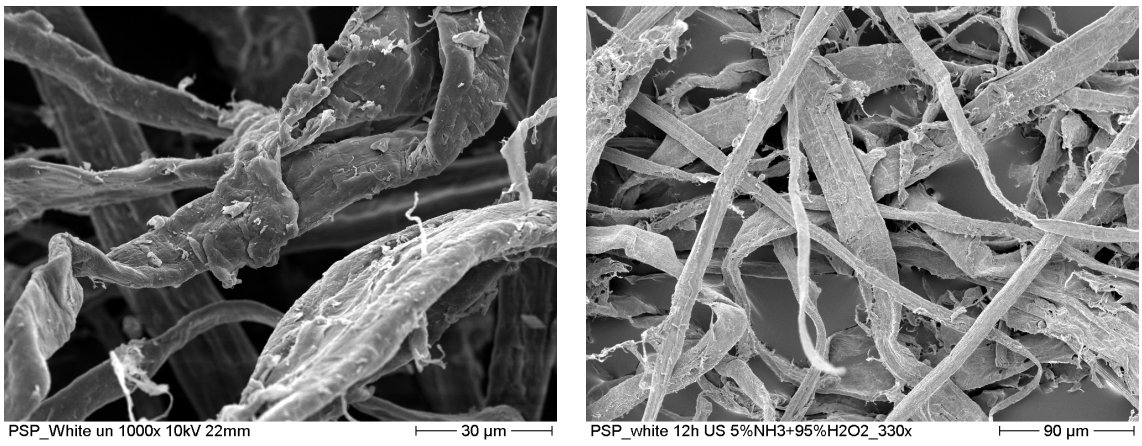
Fig. 6.2.3. Sample of cellulose Cware F 10.2 fibres.

A) Referential sample of Cware F10.2 consists of fibres with length from tens to hundreds of micrometres. Mean width of the fibres is about 20–50 µm.

B) Cware F10.2 fibres after mechanical treatment were cut in process of milling, their length is shorter and mean width of fibres is smaller.

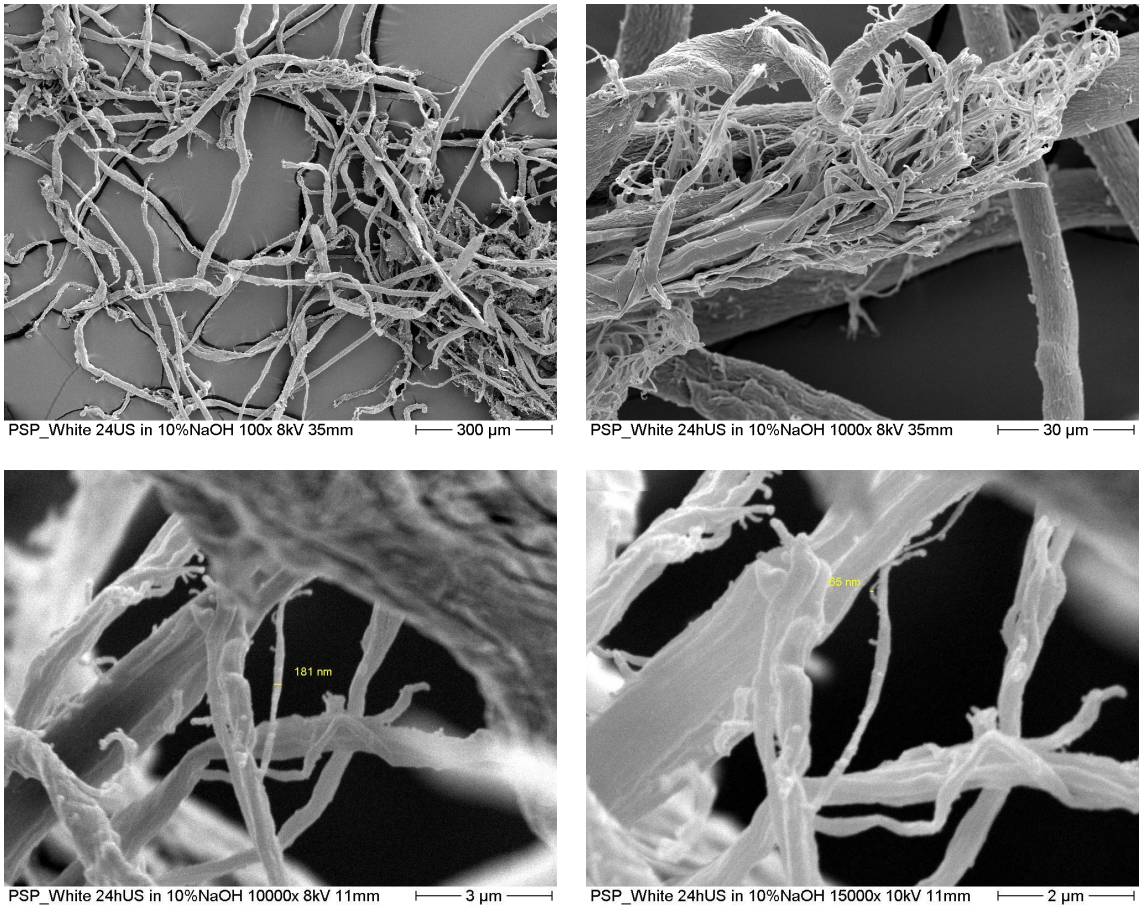
10 % solution of NaOH in distilled water, was found. This method resulted only in partial defibrillation what is demonstrated in next micrographs (Figs. 6.2.5. A–D). The mean width, as low as several hundreds nanometres, was achieved as demonstrated in Figs. 6.2.5. C and 6.2.5. D. The duration of chemical treatment was 24 hours. Additional increase of the treatment time up to 100 hours did not show any changes as can be seen from micrograph Fig. 6.2.6.

PSP-grey fibres (Fig. 6.2.7. A) were treated chemically and mechanically. Because of good results of treatment with solution of 10 % NaOH in distilled water, this chemical was used as bath for ultrasonic treatment for 24 hours. After first mechano-chemical treatment, additional treatment in homogeniser was used. This method led to the defibrillation, as it is evident from micrograph Fig. 6.2.7. B.



A) **B)**

Fig. 6.2.4. Sample of recycled cellulose PSP-white fibres.
A) Referential sample of PSP-white (length to thousand of micrometres, mean width about 30 µm).
B) PSP-white fibres after chemical treatment – bleaching by 5 % NH_3 + 95 % H_2O_2.



A) **B)**
C) **D)**

Fig. 6.2.5. Sample of PSP-white fibres after 24 hours in ultrasonic in chemical bath.
A) and **B)** Defibrillation is evident from the micrographs.
C) and **D)** Mean width, in hundreds of nm, of some defibrillated parts of fibres is in the micrograph.

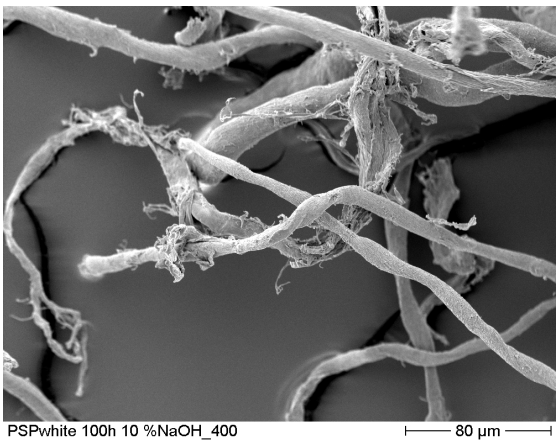
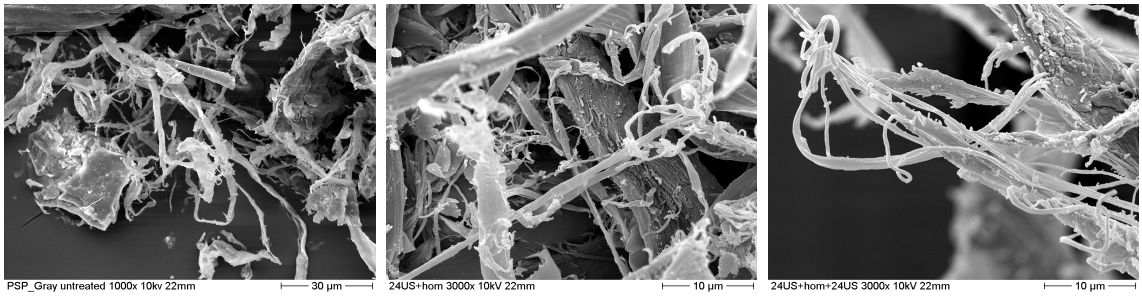


Fig. 6.2.6. Structure of defibrillated sample of PSP-white fibres after 100 hours in ultrasonic bath with 10 % NaOH.
Longer time of PSP-white fibres defibrillation with such mechano-chemical treatment did not show any additional changes in fibres morphology.

Combination of methods was tried to increase the defibrillation effect of used fibres. Af-ter first mechanical treatment, additional treatment in homogeniser was used as before and subsequently second mechano-chemical treatment in ultrasonic bath with NaOH so-lution was used again for 24 hours. Additional defibrillation is not evident in compari-son with previous processing of defibrillation (Fig. 6.2.7. C).



A) **B)** **C)**

Fig. 6.2.7. Sample of PSP-grey fibres.
A) Referential sample of PSP-grey consists of fibres with different mean length and mean width.
B) and **C)** Sample of PSP-grey fibres after 24 hours in ultrasonic in chemical bath with additional mechanical treatment in homogeniser.

Defibrillation method was expected to improve the aspect ratio of natural cellulose fi-bres. The first treated type of fibres was Cware F10.2 fibres which had homogeneous distribution of aspect ratio as it follows from charts in picture Fig. 6.2.1. Nevertheless better aspect ratio was not reached. Fibres were mainly cut without defibrillation, it can be seen in Fig. 6.2.3. For this reason the PSP fibres were chosen as fibres for experi-ments with composites. Part of treated PSP fibres by ultrasonic treatment for 24 hours in

10 % solution of NaOH in distilled water with additional mechanical treatment in homogeniser was defibrillated to submicrone size and obtained more homogeneous structure. It was suitable for following applications for composite systems in combination with soluble polyvinyl alcohol.

Because of analysis option limitation of Fibershape Systeme, treated fibres were not possible to measure and the results of defibrillation may be observed only in micrograhs (Fig. 6.2.5.). On the basis of these micrographs, the aspect ratio is at interval of 15–40.

6.3 Defibrillated Cellulose Fibres as Filler in PVA Composites

Natural cellulose fibres are suitable filler to hydrophilic polymer matrices. Cast PVA that was used in this work, changed its mechanical properties after embedding cellulose microfibrils to the dissolved matrix in distilled water. Both, the tensile strength and the Young's modulus, which are in Figs. 6.3.1. and 6.3.2., markedly decreased in comparison with pure, cast PVA.

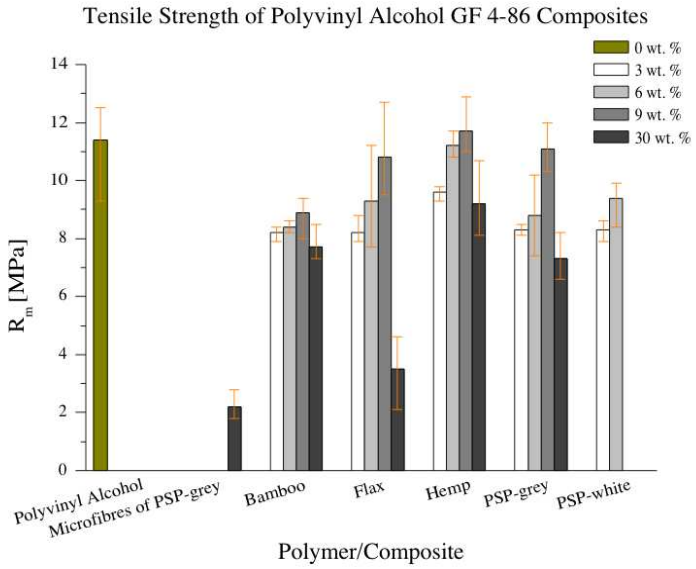


Fig. 6.3.1. Comparison of the tensile strength R_m [MPa] of cast pure polyvinyl alcohol and cast composite with PVA matrix and cellulose microfibrils as a filler and remaining made composite systems.

Tensile strength of pure PVA GF 4-86 dissolved in water decreased by 500 % after cellu-lose microfibrils were embedded into the pure PVA matrix. Large amount of cavities oc-curred in the test pieces. The explanation of the voids occurrence is in the chapter 6.1 Epoxy resin. (Table of measured values is in the Appendix C in Tab. C.2.)

The Young's modulus is in Fig. 6.3.2., in case of filled PVA with microfibrils the modulus decreased by 50 % surprisingly. (Table of measured values is in Appendix C in Tab. C.3.)

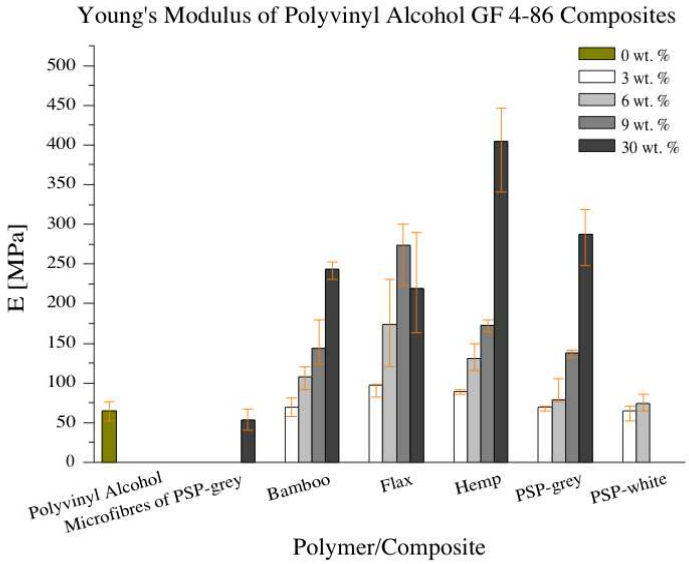
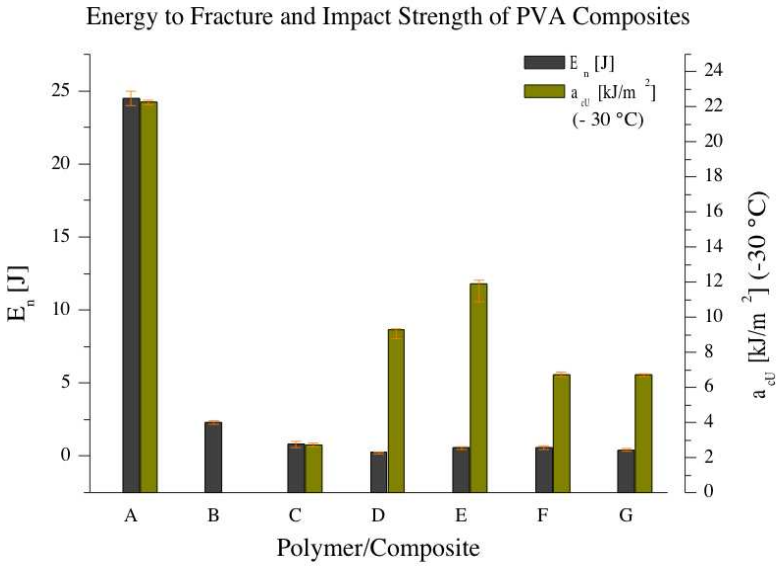


Fig. 6.3.2. Comparison of Young's modulus E [MPa] of cast pure polyvinyl alcohol and cast composite with PVA matrix and cellulose microfibrils as a filler and remaining made composite systems.

A – moulded PVA GF 4-86

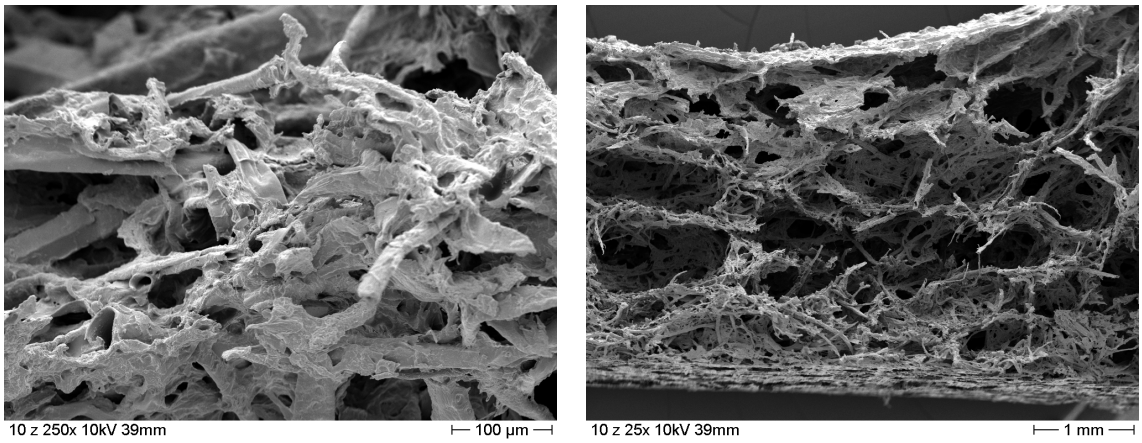


B – cast PVA GF 4-86
C – cast PVA GF 4-86 + 30 wt. % PSP-grey microfibrils
D – moulded PVA 4-88
E – moulded PVA 4-88 + 4 wt. % MAPP
F – moulded PVA 4-88 + 30 wt. % PSP-grey
G – moulded PVA 4-88 + 30 wt. % PSP-grey + 4 wt. % MAPP

Fig. 6.3.3. Fracture energy En [J] and impact strength a_{cU} [kJ/m^2] at temperature -30 °C of cast and moulded pure polyvinyl alcohol GF 4-86 and 4-88 and composite systems with these PVA matrices with 4 wt. % of MAPP or 30 wt. % of PSP-grey recycled fibres and their combination.

Figure 6.3.3. summaries the results of impact strength and fracture energy measured by Charpy method at -30 °C. The test pieces filled by microfibrils evidenced the lowest values of all the composite systems tested. Measured quantities, impact strength and energy to fracture point out the actual fact of used polyvinyl alcohol diversity. The best results were given by moulded PVA GF 4-86 – the highest impact strength – 22.3 kJ/m^2 and fracture energy – 24.5 J. Test pieces of the same material but cast, showed non-break. (Table of measured values in the Appendix C in Tab. C.4.)

The defibrillated cellulose PSP-grey fibres from recycled paper showed the worst results. All test pieces had highly inhomogeneous structure but very good adhesion – fibres were covered by PVA matrix as it can be seen from following micrographs in Fig. 6.3.4.



A) **B)**

Fig. 6.3.4. Fracture surface of cast polyvinyl alcohol GF 4-86 with 30 wt. % of PSP-grey defibrillated fibres 10 % NaOH ultrasonic bath for 24 hours.

A) and **B)** Fracture surface of cast PVA with defibrillated recycled PSP fibres shows clearly evident adhesion between fibres and matrix.

Micrograph **B)** shows general view of fracture surface of the same specimen as before. Large amount of cavities is evident in cross section area.

Defibrillation contributes to the enhancement of adhesion between fibres and polymer matrix. All the test pieces proved very good adhesion – fibres were covered by PVA ma-trix as it can be seen from micrographs in Fig. 6.3.4. Defibrillation improves also the as-pect ratio. But after embedding defibrillated fibres to the solute polymer, additional problem arises due to aglomerization of large amount of fibres and air fixation. This produced highly inhomogeneous structure. It could be explained by missing suitable processing technology and it could be an explanation for the decrease of mechanical properties. The composites with defibrillated cellulose PSP-grey fibres from recycled paper as filler showed the worst results of mechanical properties of all tested composite systems with PVA matrix. Highly different results of impact strength at temperature -30 °C and energy to fracture could be given by various chemical structure and mor-phology of tested types of composite materials.

6.4 Water Absorption of Fibres and Composites

Natural cellulose fibres used in our study are due to their chemical structure strongly hydrophilic. These hydrophilic properties of the fibres may influence the water absorption of the final composite system and also implicates problems in composites processing especially in combination with usually hydrophobic polymer matrix. The aim of this chapter was measurement of water absorption of the used cellulose fibres and to study how these fibres properties influence water absorption of final composite system.

The preliminary experiments indicate fairly rapid loss of the absorbed water. It was therefore necessary to make frequent mass measurements in early stages. The rate of absorbed water loss decreased with time (values of measurements are in Appendix D).

Epoxy resin is a hydrophobic polymer and its absorbed water content was very low, the same as by hydrophobic polypropylene. The absorbed water content (Fig. 6.4.1.) increased by 1.65–2.60 wt. % by composite systems with epoxy resin matrix with 3, 6 and 9 wt. % of PSP-grey recycled cellulose fibres as a filler. The absorbed water content increased with increasing amount of filler. (Values of this measurement are in the appendix Tab. D.1 and Tab. D.2.)

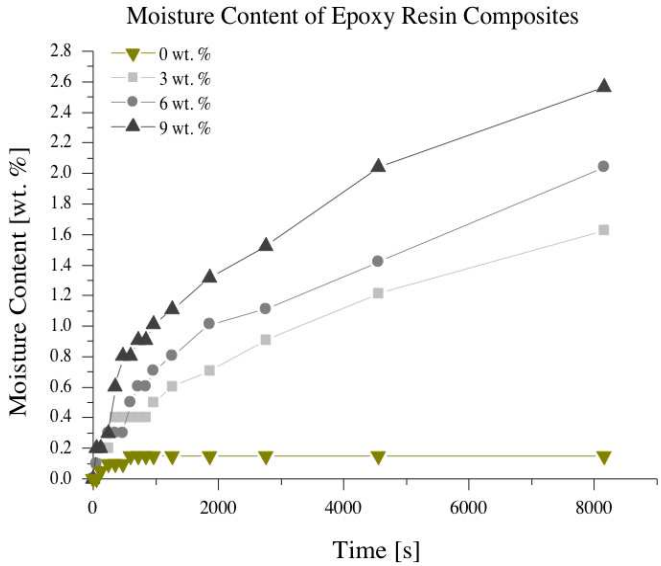


Fig. 6.4.1. Moisture content [wt. %] in dependence on drying time [s] of cast composite systems with EP matrix with 3, 6 and 9 wt. % of PSP-grey recycled cellulose fibres as a filler.

Figure 6.4.2. summarises the results of thermoplastic polymer – polypropylene. PP is hydrophobic polymer and its absorbed water content was very low. The absorbed water content increased by 2.1 wt. % by addition of 30 wt. % of PSP-grey recycled cellulose fibres. This value decreased by 1 wt. % by addition of 4 wt. % of MAPP to the previous composite system. (Values of this measurement are in the appendix Tab. D.3 and Tab. D.4.)

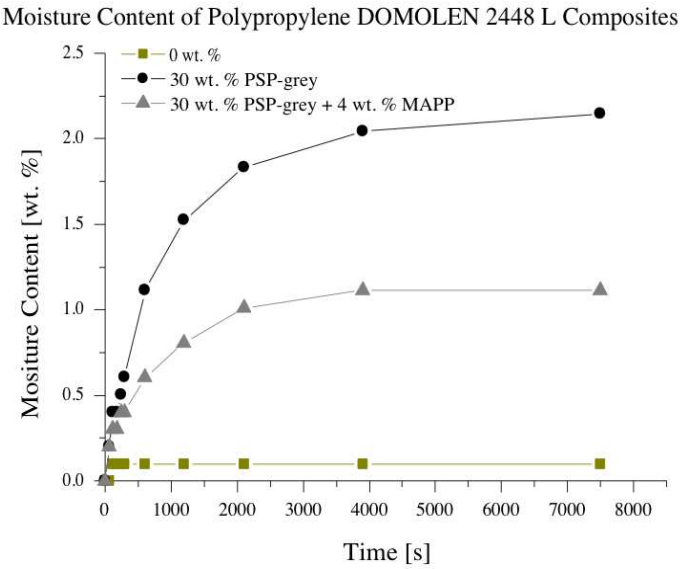
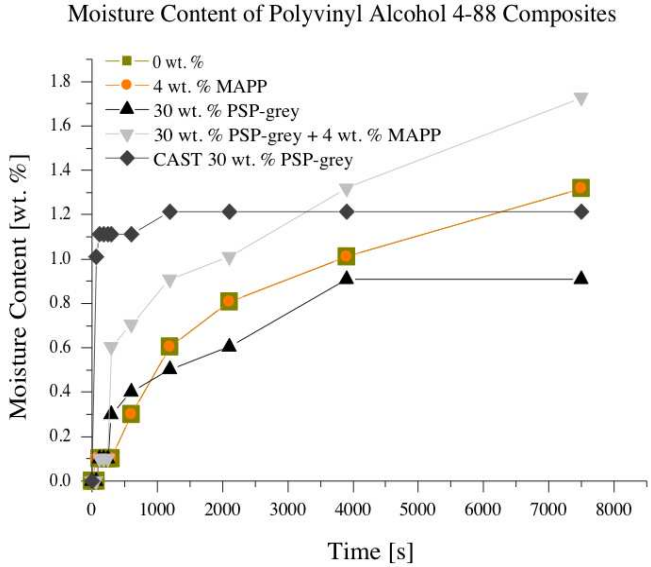


Fig. 6.4.2. Moisture content [wt. %] in dependence on drying time [s] of pure injection moulded polypropylene and composite systems with 30 wt. % of PSP-grey recycled cellulose fibres and 30 wt. % of PSP-grey fibres together with 4 wt. % of MAPP as filler.

Atmospheric humidity, and not from water environment, was measured in case of composites with PVA matrix – because of polymer hydrosolubility. Results of absorbed water content of injection moulded and cast polyvinyl alcohol 4-88 are in Fig. 6.4.3. The content of absorbed water was about 2 wt. %. Moulded test pieces of pure PVA 4-88 and PVA 4-88 with 4 wt. % of MAPP had almost identical time response. (Values of this measurement are in the appendix Tab. D.5 and Tab. D.6.)

Fig. 6.4.3. Moisture content [wt. %] in dependence on drying time [s] of pure moulded polyvinyl



alcohol 4-88 and composite systems with 4 wt. % of MAPP or 30 wt. % of PSP-grey recycled cellulose fibres as a filler and their combination. Cast PVA 4-88 with 30 wt. % of PSP-grey fibres is for comparison in the chart.

Cast polyvinyl alcohol GF 4-86, results are in Fig. 6.4.4., had greater absorbed water content – 4.5 wt. % in case of addition of 30 wt. % of PSP-grey cellulose fibres to the matrix. Method of test pieces processing did not have significant influence on water absorption. The absorbed water content was 2.5–3.0 wt. %.

Difference was found between PVA GF 4-86 and PVA 4-88, both with 30 wt. % of PSP-grey fibres. The absorbed water content of PVA 4-88 was 1.25 wt. % and it was the lowest value. Cast test pieces of PVA 4-88 had faster loss of moisture content in early stages

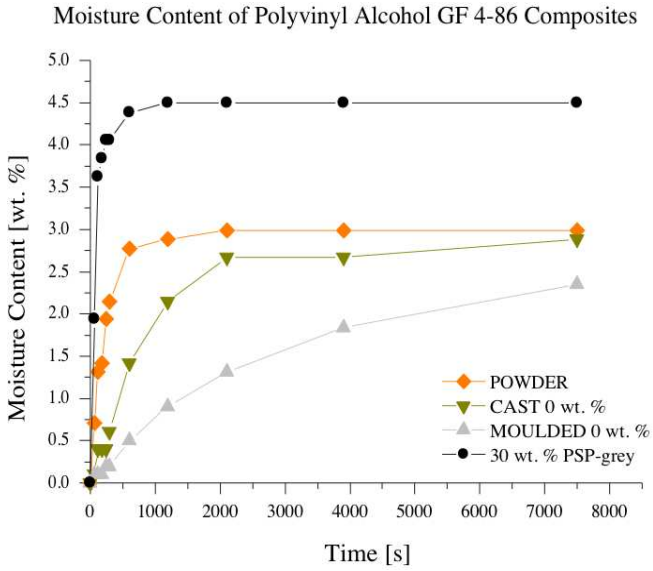


Fig. 6.4.4. Moisture content [wt. %] in dependence on drying time [s] of pure, cast and injection moulded polyvinyl alcohol with and without filler. PVA GF 4-86 and PVA 4-88, both with 30 wt. % of PSP-grey recycled cellulose fibres, are for comparison in one chart.

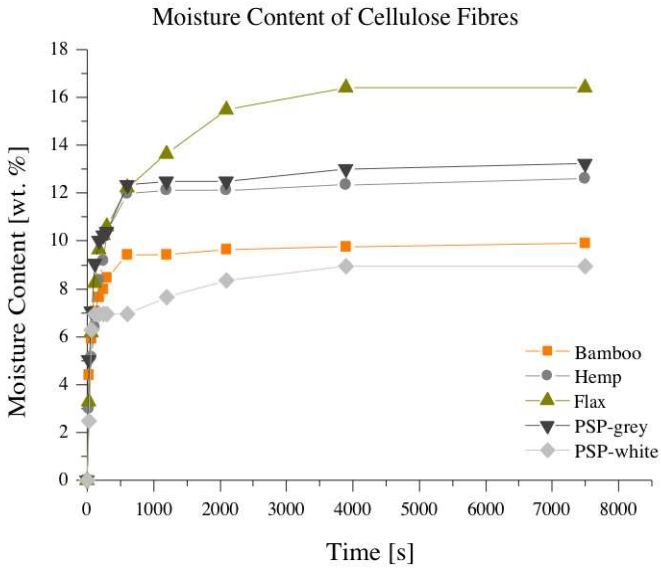


Fig. 6.4.5. Dependence of moisture content [wt. %] on drying time [s] of used fillers from natural cellulose fibres.

of conditioning than injection moulded test pieces. (Values of this measurement are in the appendix Tab. D.7 and Tab. D.8.)

Results of water absorption measured for all of the cellulose fibres used in our study are summarised in Fig. 6.4.5. The absorbed water content of natural cellulose fibres varied between 9 wt. %, for PSP-white fibres, and 16.5 wt. %, in case of flax fibres. (All the values of this measurement are attached in the appendix Tab. D.9 and Tab. D.10.)

Epoxy resin and polypropylene as hydrophobic polymers had low water absorption. The water absorption increased with increasing filling fraction of embedded cellulose fibres. Embedded PSP-grey fibres enhanced water absorption by 2 500 %, in case of EP with 9 wt. % of fibres, and by 2 100 %, in case of PP with 30 wt. % of PSP fibres. These results could be explained by presence of large amount of cavities in test pieces that could cause easier water absorption [81, 82]. MAPP coupling agent addition lessens water absorption, which could probably be due to reduction of capillary interstices between cellulose fibres and polymer matrix.

Water absorption of both tested pure PVAs was in interval 1.3–2.4 wt. %. The highest water absorption acquired PVA composites – increase onto 1.7–4.5 wt. %. The tested composite systems had the same character and after 1000 seconds happened to deceleration. Major deceleration of water absorption occurred at moulded test pieces, this could happen due to influence of structure and voids number reduction resulting from preparation method. Cast test pieces made from solution of polymer in distilled water were the most deliquescent. The difference between PVA GF 4-86 and PVA 4-88, that flows from Fig.6.4.6. was especially interesting. Sharp growth and subsequent stabilisation of

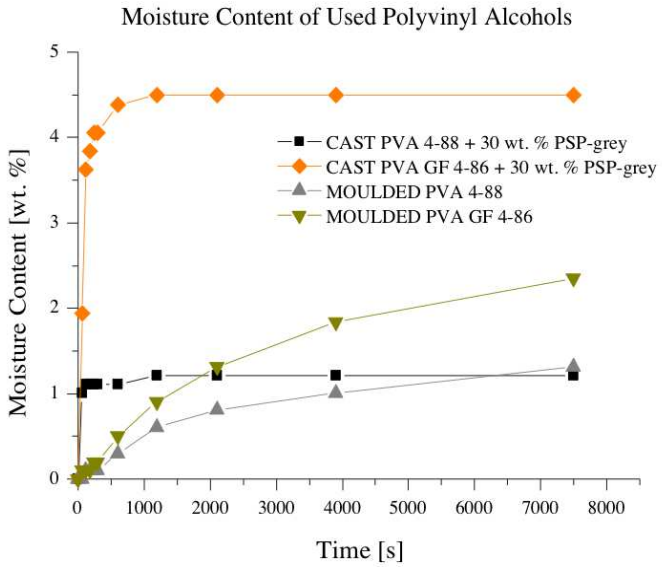


Fig. 6.4.6. Comparison of water absorption of used types of PVA – GF 4-86 and 4-88 with and without MAPP coupling agent.

water absorption occurred at first moments of PVA GF 4-86 measurement. Gradual increase of PVA 4-88 softly differs and there is less water absorption. It could have happened due to their different structure. Because of hydrophilic nature of polyvinyl alcohol the increase of water absorption was not so significant after incorporating cellulose fibres as in case of hydrophobic polypropylene and epoxy resin.

Absorbed water content by weight of natural cellulose fibres was between 9 wt. %, in case of PSP-white fibres, and 16.5 wt. %, in case of flax fibres. Lower water absorption of PSP-white fibres from recycled paper could be probably explained by bleaching chemical pretreatment of these fibres.

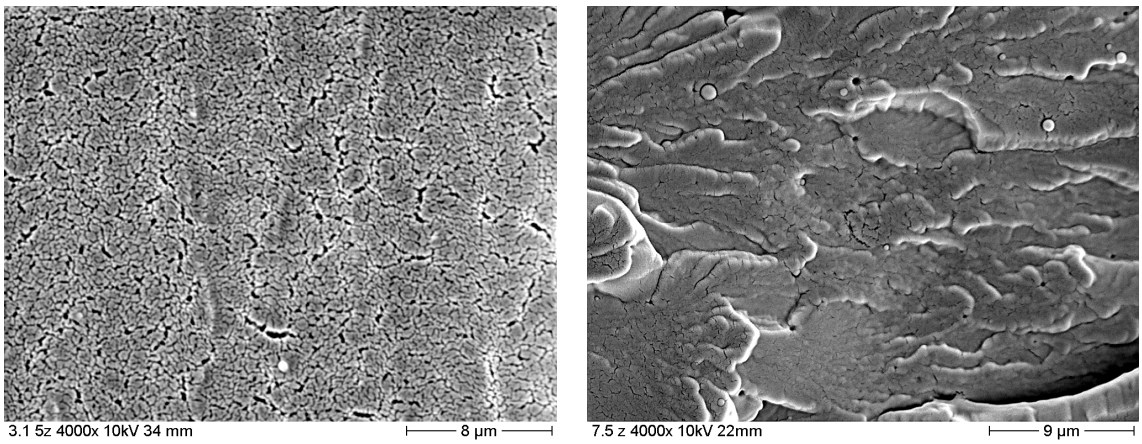
7 Concluding Remarks

This research work is focused on study of characterisation and utilisation of natural cellulose fibres and microfibres in composite systems with polymer matrices.

In order to characterise the selected systems, three main streams of studies were followed: measurement of mechanical properties (tensile strength, Young's modulus), defibrillation of natural cellulose fibres and water absorption of fibres and of complete composites. Three types of polymer matrix were selected: epoxy resin (EP) representing hydrophobic thermosets and from thermoplastic polymers hydrophobic polypropylene (PP) and hydrophilic polyvinyl alcohol (PVA). From the produced cellulose fibres bamboo, flax, hemp, and recycled paper were selected as filler. According to our knowledge, there has not been published paper dealing with composite material with recycled paper.

Evaluation of tensile strength and Young's modulus in dependence on fibres type and their amount were measured on the basis of tensile test. Homogeneity of prepared test pieces and adhesion between fibres and polymer matrix were checked by scanning electron microscopy. The wetting behaviour of the natural cellulose fibres and composite systems containing such fibres as a filler were characterised by measuring its initial and final mass. At least 7 test pieces were prepared from each composite material for each type of mechanical testing.

Test pieces with EP matrix were cast. PP test pieces were extruded with subsequent injection moulding. Composites with PVA matrix were cast from 20 % water solution of polymer in distilled water. Two types of PVA were used in this work – PVA GF 4-86 (copolymer) and PVA 4-88 (homopolymer). Solubility of both polymers was the same,



A) B)

Fig. 7.1. A) Fracture surface of polyvinyl alcohol GF 4-86 processed by injection moulding.
B) Fracture surface of polyvinyl alcohol 4-88 processed by injection moulding.

but their water absorption and mechanical properties were different due to chemistry and morphology (it is evident from the micrographs Fig. 7.1.). These types of materials were injection moulded with difficulties and the producer did not recommend this type of processing method and describes it as impossible [29]. The injection moulding of PVA was accomplished due to the possibility to compare the test pieces made from PVA with other test pieces of composite systems produced by the same technology.

Original basic research results in characterisation of mechanical properties of composite systems with hydrophilic natural cellulose fibres as a filler (in the filling fraction 3 wt. %, 6 wt. %, 9 wt. % and 30 wt. %) and hydrophilic or hydrophobic polymer matrices were obtain. The filling fraction strongly influences properties of resulting composite systems. The Young's modulus increased with the increase of filling fraction. Such behaviour was observed in more cases [4, 9, 14, 39, 43, 86] but almost all increases from our experiments were lower compared with literature. The lower values of mechanical properties were attributed to fibre-fibre interaction, voids and dispersion problems in the article [87]. Our experiments proved that filling fraction should to be restricted in case of cast methods and that fibre-matrix interaction is very important also.

Generally, hydrophilic cellulose fibres do not adhere well to hydrophobic polymers. In the materials group of natural fibre-reinforced thermosetting plastics, especially in the group of natural fibre-reinforced epoxy resins, there is only a little knowledge about the influence of suitable coupling agents on the parameters of composites in comparison with natural fibre and reinforced thermoplastics [9, 21, 88] and we did not use any in experiments with EP composites. Coupling agents had been widely used to improve the bonding between various cellulose fibres and thermoplastic polymer matrices [4, 12, 19, 39, 88–90]. Many studies were concerned with the effectiveness of maleic-anhydride grafted polypropylene as a coupling agent [4, 19, 39, 88, 89]. The effect of natural plant fibres on the tensile strength and Young's modulus was poor when there was no coupling agent as in our experiments. In literature is shown that the addition of MAPP as coupling agent improved the composite performance by enhancing the adhesion between cellulose fibres and PP. This enhancement we proved also in our experiments. Behaviour of MAPP as plasticiser was demonstrated in our research work among others.

Most of the investigations in this field have dealt with the effects of chemical treatment by coupling agents as it is possible to see above and a number of research papers is interested in plasma modification of natural fibres surfaces [19, 42, 43, 90]. Unlike these published investigations we tried to modify surface of PP polymer matrix in our experiments in air- or oxygen-plasma. Both plasma treatments did not improve the tensile strengths and Young's modulus of cellulose fibre-PP composites in our experiments. And the influence of plasma treatments on adhesion was rather negative, in spite of the fact that adhesion of plasma treated polymers to metals was good as was shown in [85]. It is obvious that affection of polymer particles surface layer in consequence of its interaction with plasma respectively with plasma radiation happened and this problem should be study further.

Consequent selection of the topics was based on the fact that defibrillated and nondefibrillated cellulose fibres as well in combination with degradable polyvinyl alcohol matrix could have potential of use as fully biodegradable composite systems.

Our method of defibrillation was expected to improve the aspect ratio of cellulose fibres and adhesion also. Part of treated PSP fibres after mechano-chemical treatment was defibrillated to submicrone size and it was suitable for following applications for composite systems in combination with soluble polyvinyl alcohol in the experiments.

From microscopic point of view it could be said that adhesion of polymer matrix to fibre is outright better both in case of fibres defibrillation in connection with thermoplastic hydrophilic polyvinyl alcohol matrix where the defibrillation method improved aspect ratio of fibres and in case of usage of maleic anhydride grafted polypropylene in connection with thermoplastic hydrophobic polypropylene matrix too. The improvement of adhesion, in case of PVA composites, does not display consistent results in mechanical properties, especially where good adhesion is found – from macroscopic point of view comparison of measured values does not manifest it. Occurrence of voids leads to reduction of cross section. High amount of voids abounds in almost all prepared test pieces. Fig. 7.2. shows significant adhesion between natural cellulose fibres and polymer matrix including large amount of voids and inhomogeneities. On the contrary from literature when are processed thin films and foils with defibrillated fibres low abundance of voids can be found [9, 10, 14–16, 21, 91].

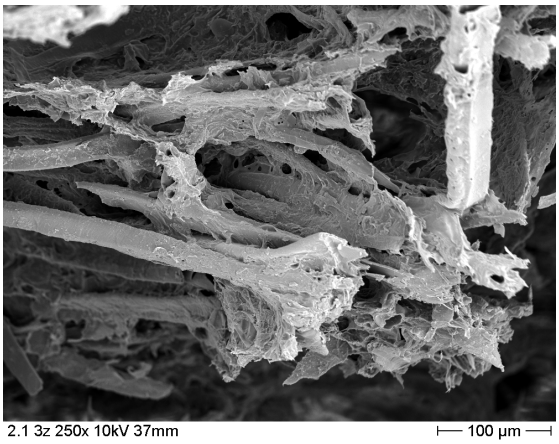


Fig. 7.2. Fracture surface of cast PVA GF 4-86 with 30 wt. % of defibrillated recycled PSP fibres shows clearly evident adhesion between fibres and matrix.

PVA composites with defibrillated microfibres had lower measured values in comparison with pure PVA matrix in all cases. It is essential to improve methodology of preparation in case of defibrillated fibres, and accumulated air in defibrillated parts of fibres and agglomerates of fibres due to the strong fibre-fibre interactions resulting from strong intermolecular hydrogen bonding [19, 43] remove. Occurrence of these imperfections explains better mechanical properties by moulded composite systems. It has already shown in the literature [19, 43, 92, 93] that the heterogeneous distribution of the reinforcements within the matrix could have consequences on the mechanical properties of the composites.

Next topic which was studied in our research work is water absorption of composites. All polymer composites absorb moisture in humid atmosphere and when immersed in wa-

ter [93] and methodology of preparation influences water absorption of produced composites also as was shown in our experiments. The water absorption increases as the fibre filling fraction increases, that was proved in our experiments, due to the high cellulose content [4, 6, 9, 11, 15 19, 20, 67, 93].

The results of the work clearly show significant influence of natural plant fibres in composite systems. These fibres could be used to increase mechanical properties and they could replace artificial fibres in polymer matrices.

An interesting concept is not only the possibility of using coupling agent, which permit connection between hydrophilic fibres and hydrophobic matrix, but also tried usage of the large specific surface of fibres, which could be acquired by chemical and mechanical treatment. Plasma treatment of polymers is not a suitable method for connecting hydrophilic cellulose fibres with hydrophobic polymer matrix. Connection of these fibres with epoxy resin is also not favourable.

This thesis maps and characterises usage of natural cellulose fibres in composite systems with polymer matrices. This is the first integrated work of a new direction in the Czech Republic that uses defibrillated recycled paper as a filler, recycled paper in connection with polypropylene as matrix, coupling agent in composites with polyvinyl alcohol matrix together with injection moulding and plasma treatment of polypropylene for connection with cellulose fibres.

8 Conclusion

Composite systems made from hydrophobic thermosetting and hydrophobic and hydrophilic thermoplastic polymers with filler from natural cellulose fibres prepared by different technologies were investigated. Mechanical properties of composite systems and pure polymers in dependence on filling fraction were measured.

1. Dependence was proved according to the theory in majority cases. According SEM, discrepancies were assigned to formation of voids and agglomerates.
2. Tensile strength and Young's modulus were measured. Dependence on filling fraction of these properties was observed. Homogenisation of produced composite systems that was influenced by processing method significantly impacted mechanical properties of the systems. Extrusion followed by injection moulding was superior to cast method.
3. Technology of natural cellulose fibres defibrillation was developed. Improvement of aspect ratio and overall adhesion of cellulose fibres to polymer matrix was proved. Test pieces of composite systems were prepared and possibility of utilisation of the cellulose fibrils in polymer matrix was verified.
4. Water absorption of composite systems, pure polymers and natural cellulose fibres was measured and negative influence of incorporated natural cellulose fibres to the polymer matrices, which increases water absorption of resulting composites, was evidenced.

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Symbol Table

a_{cU}	Impact Strength
E	Young's Modulus
En	Energy to Fracture
EP	Epoxy Resin
M	Absorbed Water Content
MA	Maleic Anhydride
MAPP	Maleic Anhydride Grafted Polypropylene
M_e	Molecular Weight
M_n	Number Average Molecular Weight
M_w	Weight Average Molecular Weight
PE	Polyethylene
PECVD	Plasma Enhanced Chemical Vapour Deposition
PP	Polypropylene
P_n	Degree of Polymerisation
PVA	Polyvinyl Alcohol
R_m	Tensile Strength
T_g	Glass Transition Temperature
w_{dry}	Weight of Wet Sample
w_{wet}	Weight of Dry Sample

Appendix A

Tables of Measured Values of Epoxy Resin

Tab. A.1
Values of tensile strength of cast composite systems with epoxy resin matrix and different cellulose fibres as a filler and its filling fraction

R_m [MPa]	Bamboo	Flax	Hemp	PSP-grey
3 wt. %	41.28	42.80	54.17	45.67
6 wt. %	56.61	40.61	51.19	42.13
9 wt. %	51.82	39.40	40.94	33.46

Tab. A.2
Values of Young's modulus of cast composite systems with epoxy resin matrix and different cellulose fibres as a filler and its filling fraction

E [MPa]	Bamboo	Flax	Hemp	PSP-grey
3 wt. %	1 055	1 225	1 356	932
6 wt. %	1 404	1 362	1 387	959
9 wt. %	1 567	1 432	1 410	984

Appendix B

Tables of Measured Values of Polypropylene

Tab. B.1
Mechanical properties of pure polymer and composite with polypropylene DOMOLEN 2448 L matrix

Polymer/Composite	R_m [MPa]	E [MPa]
PP	17.1	674.9
PP + 4 wt. % MAPP	21.9	1 220.9
PP + 30 wt. % PSP-grey	20.7	2 530.0
PP + 4 wt. % MAPP + 30 wt. % PSP-grey	34.7	2 350.2

Tab. B.2
Values of tensile strength of composite systems with polypropylene BE170MO matrix and different cellulose fibres (bamboo, hemp) as a filler and its filling fraction, one group of composites was with PP matrix treated by oxygen plasma, the second with air plasma

R_m [MPa]	pure PP	Bamboo	Hemp	PP - oxy	Bamboo	Hemp	PP - air	Bamboo	Hemp
0 wt. %	25			25			24		
9 wt. %		18	17		18	16		17	18
30 wt. %		14	17		14	13		15	14

Tab. B.3
Values of Young's modulus of composite systems with polypropylene BE170MO matrix and different cellulose fibres (bamboo, hemp) as a filler and its filling fraction, one group of composites was with PP matrix treated by oxygen plasma, the second with air plasma

E [MPa]	pure PP	Bamboo	Hemp	PP - oxy	Bamboo	Hemp	PP - air	Bamboo	Hemp
0 wt. %	1 290			1 290			1 280		
9 wt. %		1 420	1 390		1 420	1 270		1 340	1 420
30 wt. %		1 730	1 190		1 760	1 790		1 770	1 830

Appendix C

Tables of Measured Values of Polyvinyl Alcohol

Tab. C.1
Mechanical properties of pure polymer and composite with Polyvinyl alcohol 4-88 matrix

Polymer/Composite	R_m [MPa]	E [MPa]
PVA	43.8	6 485.6
PVA + 4 wt. % MAPP	56.9	3 595.3
PVA + 30 wt. % PSP-grey	65.4	4 375.5
PVA + 4 wt. % MAPP + 30 wt. % PSP-grey	57.9	6 674.7

Tab. C.2
Values of tensile strength of cast composite systems with polyvinyl alcohol matrix and different cellulose fibres as a filler and its filling fraction

R_m [MPa]	Bamboo	Flax	Hemp	PSP-grey	Microfibres of PSP-grey	PSP-white
3 wt. %	8.2	8.2	9.6	8.3	–	8.3
6 wt. %	8.4	9.3	11.2	8.8	–	9.4
9 wt. %	8.9	10.8	11.7	11.1	–	–
30 wt. %	7.7	3.5	9.2	7.3	1.9	–

Tab. C.3
Values of Young's modulus of cast composite systems with polyvinyl alcohol matrix and different cellulose fibres as a filler and its filling fraction

E [MPa]	Bamboo	Flax	Hemp	PSP-grey	Microfibres of PSP-grey	PSP-white
3 wt. %	69	97	89	70	–	65
6 wt. %	108	174	131	79	–	74
9 wt. %	144	274	173	138	–	–
30 wt. %	243	219	405	287	27	–

Tab. C.4
Impact strength and fracture energy of polyvinyl alcohol GF 4-86 and 4-88

Polymer/Composite	En [J]	a_{cU} [kJ/m^2] (-30°C)
moulded PVA GF 4-86	24.5	22.3
cast PVA GF 4-86	2.3	nonbreak°
cast PVA GF 4-86 + 30 wt. % PSP-grey microfibrils*	0.1	2.7
moulded PVA 4-88	0.3	9.3
moulded PVA 4-88 + 4 wt. % MAPP	0.6	11.9
moulded PVA 4-88 + 30 wt. % PSP-grey	0.6	6.7
moulded PVA 4-88 + 30 wt. % PSP-grey + 4 wt. % MAPP	0.4	6.7

* after 24 hours in 10 % NaOH ultrasonic bath
° This state was occurred because of test piece geometry that was only 2mm thick.

Appendix D

Tables of Measured Values of Water Absorption

Tab. D.1
Loss of moisture content of cast composite systems with EP matrix with 3, 6 and 9 wt. % of PSP-grey recycled cellulose fibres as a filler (time interval 0–720 seconds)

Composite	0 [s]	60 [s]	120 [s]	240 [s]	360 [s]	480 [s]	600 [s]	720 [s]
3 wt. % PSP-grey	1.000	0.999	0.998	0.998	0.996	0.996	0.996	0.996
6 wt. % PSP-grey	1.000	0.999	0.998	0.997	0.997	0.997	0.995	0.994
9 wt. % PSP-grey	1.000	0.998	0.998	0.997	0.994	0.992	0.992	0.991

Tab. D.2
Loss of moisture content of cast composite systems with EP matrix with 3, 6 and 9 wt. % of PSP-grey recycled cellulose fibres as a filler (time interval 840–8 160 seconds)

Composite	840 [s]	960 [s]	1 260 [s]	1 860 [s]	2 760 [s]	4 560 [s]	8 160 [s]
3 wt. % PSP-grey	0.996	0.995	0.994	0.993	0.991	0.988	0.984
6 wt. % PSP-grey	0.994	0.993	0.992	0.990	0.989	0.986	0.980
9 wt. % PSP-grey	0.991	0.990	0.989	0.987	0.985	0.980	0.975

Tab. D.3
Loss of moisture content of moulded pure polymer PP and moulded composite systems with PP matrix with 30 wt. % of PSP-grey recycled cellulose fibres and 30 wt. % of PSP-grey fibres together with 4 wt. % of MAPP as a filler (time interval 0–300 seconds)

Polymer/Composite	0 [s]	60 [s]	120 [s]	180 [s]	240 [s]	300 [s]
PP	1.000	1.000	0.999	0.999	0.999	0.999
PP + 30 wt. % PSP-grey	1.000	0.998	0.996	0.996	0.995	0.994
PP +30 wt. % PSP-grey + 4 wt. % MAPP	1.000	0.998	0.997	0.997	0.996	0.996

Tab. D.4
Loss of moisture content of moulded pure polymer PP and moulded composite systems with PP matrix with 30 wt. % of PSP-grey recycled cellulose fibres and 30 wt. % of PSP-grey fibres together with 4 wt. % of MAPP as a filler (time interval 600–7 500 seconds)

Polymer/Composite	600 [s]	1 200 [s]	2 100 [s]	3 900 [s]	7 500 [s]
PP	0.999	0.999	0.999	0.999	0.999
PP + 30 wt. % PSP-grey	0.989	0.985	0.982	0.980	0.979
PP +30 wt. % PSP-grey + 4 wt. % MAPP	0.994	0.992	0.990	0.989	0.989

Tab. D.5
Loss of moisture content of moulded pure polymer PVA 4-88 and moulded composite systems with PVA 4-88 matrix with 4 wt. % of MAPP or 30 wt. % of PSP-grey recycled cellulose fibres as a filler and their combination (time interval 0–300 seconds)

Polymer/Composite	0 [s]	60 [s]	120 [s]	180 [s]	240 [s]	300 [s]
PVA 4-88	1.000	1.000	0.999	0.999	0.999	0.999
PVA + 4 wt. % MAPP	1.000	0.999	0.999	0.999	0.999	0.999
PVA + 30 wt. % PSP-grey	1.000	1.000	0.999	0.999	0.999	0.997
PVA + 30 wt. % PSP-grey + 4 wt. % MAPP	1.000	1.000	0.999	0.999	0.999	0.994
PVA + 30 wt. % PSP-grey cast	1.000	0.990	0.989	0.989	0.989	0.989

Tab. D.6
Loss of moisture content of moulded pure polymer PVA 4-88 and moulded composite systems with PVA 4-88 matrix with 4 wt. % of MAPP or 30 wt. % of PSP-grey recycled cellulose fibres as a filler and their combination (time interval 600–7 500 seconds)

Polymer/Composite	600 [s]	1 200 [s]	2 100 [s]	3 900 [s]	7 500 [s]
PVA 4-88	0.997	0.994	0.992	0.990	0.987
PVA + 4 wt. % MAPP	0.997	0.994	0.992	0.990	0.987
PVA + 30 wt. % PSP-grey	0.996	0.995	0.994	0.991	0.989
PVA +30 wt. % PSP-grey + 4 wt. % MAPP	0.993	0.991	0.990	0.987	0.983
PVA + 30 wt. % PSP-grey cast	0.989	0.988	0.988	0.988	0.988

Tab. D.7
Loss of moisture content of pure polymer PVA GF 4-86 and composite systems with PVA GF 4-86 or PVA 4-88 matrix with 30 wt. % of PSP-grey recycled cellulose fibres as a filler (time interval 0–300 seconds)

Polymer/Composite	0 [s]	60 [s]	120 [s]	180 [s]	240 [s]	300 [s]
PVA – powder	1.000	0.993	0.987	0.986	0.981	0.979
PVA – cast	1.000	0.999	0.996	0.996	0.996	0.994
PVA – moulded	1.000	0.999	0.999	0.999	0.998	0.998
PVA GF 4-86 + 30 wt. % PSP-grey	1.000	0.981	0.965	0.963	0.961	0.961
PVA 4-88 + 30 % wt. PSP-grey	1.000	0.990	0.989	0.989	0.989	0.989

Tab. D.8
Loss of moisture content of pure polymer PVA GF 4-86 and composite systems with PVA GF 4-86 or PVA 4-88 matrix with 30 wt. % of PSP-grey recycled cellulose fibres as a filler (time interval 600–7 500 seconds)

Polymer/Composite	600 [s]	1 200 [s]	2 100 [s]	3 900 [s]	7 500 [s]
PVA – powder	0.973	0.972	0.971	0.971	0.971
PVA – cast	0.986	0.979	0.974	0.974	0.972
PVA – moulded	0.995	0.991	0.987	0.982	0.977
PVA GF 4-86 + 30 % wt. PSP-grey	0.958	0.957	0.957	0.957	0.957
PVA 4-88 + 30 wt. % PSP-grey	0.989	0.988	0.988	0.988	0.988

Tab. D.9
Loss of moisture content of used natural cellulose fibres (time interval 0–240 seconds)

Fibre	0 [s]	30 [s]	60 [s]	120 [s]	180 [s]	240 [s]
Bamboo	1.000	0.958	0.944	0.934	0.929	0.926
Hemp	1.000	0.971	0.951	0.940	0.923	0.916
Flax	1.000	0.968	0.942	0.924	0.912	0.907
PSP-grey	1.000	0.952	0.934	0.917	0.909	0.907
PSP-white	1.000	0.976	0.941	0.935	0.935	0.935

Tab. D.10
Loss of moisture content of used natural cellulose fibres (time interval 300–7 500 seconds)

Fibre	300 [s]	600 [s]	1 200 [s]	2 100 [s]	3 900 [s]	7 500 [s]
Bamboo	0.922	0.914	0.914	0.912	0.911	0.910
Hemp	0.906	0.893	0.892	0.892	0.890	0.888
Flax	0.904	0.891	0.880	0.866	0.859	0.859
PSP-grey	0.906	0.890	0.889	0.889	0.885	0.883
PSP-white	0.935	0.935	0.929	0.923	0.918	0.918