MECHANICAL PROPERTIES OF BIOPOLYMER COMPOSITE WITH NATURAL FIBERS SURFACE MODIFIED BY LOW-TEMPERATURE PLASMA

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DOI : 10.17973/MMSJ.2020_10_2020039

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The paper deals with the evaluation of mechanical properties of a biopolymer composite, where a low temperature plasma, atmospheric dielectric barrier discharge (DBD) physical treatment was used to improve adhesion at the interface between polymer and natural fibers. The polymer composite matrix was PLA polymer from NatureWorks LLC. The reinforcing filler were natural coconut fibers, which were in three weight percentage in the composite system. Tests of evaluation of mechanical properties, tensile and bending test and impact strength test and differential scanning calorimetry were performed on prepared samples. Electron microscopy was used to evaluate the effect of plasma treatment on the surface of natural fibers as well as adhesion at the interface between fibers and matrix. Experimental results of mechanical properties confirmed that the use of plasma surface treatment of natural coconut fibers using DBD technology influences the final properties of biocomposites.

KEYWORDS

Biocomposite, PLA, natural fibers, coconut, Plasma

1 INTRODUCTION

Polymeric materials and their composites are currently one of the most progressively developing materials, and there is no doubt that they are essential for a modern technical society. Recently, environmental research and development has been increasingly focusing on the use of natural materials. Nowadays, it is possible to use natural material not only as composite matrices (biopolymers) but also as natural fibers, replacing synthetic fibers. The growing interest in natural fibers is mainly thanks to their good mechanical properties, low density and biodegradability at the end of their life cycle, and low production costs. For the factors given above, it is implied that the cost of obtaining natural fibers is three times lower than glass fibers, four times lower than aramid fibers and five times lower than carbon fibers [Kalia 2011].

Fibers of plant origin are cell walls occurring in the stems and leaves of plants. The fiber is an elementary linear shape, it has a characteristic longitudinal and cross-section, and consists of primary chemical components. Fibers consist of cellulose, hemi-cellulose, lignin, aromatics, waxes and other lipids, ash and water-soluble compounds [Mohanty 2005]. In this respect, plant natural fibers are an optimized structure, tested by the evolution. Compared to glass or carbon fiber processing, natural fibers have a better environmental and safety impact when using natural fiber products. The disadvantage is flammability, variable product quality as well as the need for drying.

Poly (lactic acid) (PLA) as a bio-based, biodegradable and biocompatible thermoplastic with high strength (50-70 MPa) and modulus (3 GPa) still faces important industrial problems such as a slow crystallization, inherent brittleness and low impact resistance to compete with synthetic commodity polymers.

Products based on the use of natural polymers and fibers are becoming increasingly important. In the case of PLA-based biocomposites, two important sectors can be distinguished, in which products are used, especially, in medical and technical applications.

The use of biocomposites and natural fibers offers broad opportunities for technical innovations as well as for sustainable development. Today, it is no longer just biodegradable packaging, foil and disposable products, but also various technical products such as furniture components. Lately, there has been a strong demand for these composites, especially in the automotive industry. The automotive industry is gradually gaining a leading role in the use of natural fiber composites. Particularly, it refers to unsighted interior parts, such as the air filter cover made by Röchling Automotive that is PLA-based biocomposite as well as exterior body parts [Müssig 2010]. Another industry, where biocomposites will definitely find widespread use in the future is electronics manufacturing. The Finnish company Nokia was the first one to make several types of mobile phones from a biocomposite based on PLA. Likewise, some computer manufacturers are starting to use mostly PLA-based biocomposites, such as Fujitsu, a Japanese company.

Final properties of PLA composites reinforced with natural fibers are influenced by several factors, both in fiber terms as well as matrix terms. From the fiber point of view, the impact is carried out by the degree of filling, fiber length, fiber morphology, fiber orientation and fiber distribution. From the PLA matrix perspective, the resulting properties depend on the molecular weight or also on the residual lactide content and processing conditions. There had been conducted several experiments in the past, such as with PLA wood fiber. It had been detected that the tensile strength did not improve after the injection, even at a filling level of 20 to 40 %. These results were ascribed to poor fiber distribution in the PLA matrix and to insufficient adhesion at the fiber-matrix interface [Mweikambo 2006]. The natural fiber surfaces are generic hydrophilic and PLA matrices are hydrophobic. It causes poor interfacial bonding between both components. One of the possible ways how to influence mechanical properties of biocomposite materials is through chemical modification of the polymer matrix, which leads to an improvement of the interfacial adhesion. Another possibility how to influence final properties of PLA composites with natural fibers is to modify the fiber surface by a physical or chemical way.

Thanks to short treatment time, Physical plasma bring low operation cost [Adeniyi 2019] and the promising technology of natural fiber surface modification. The effect of physical treatments to natural fibers consists of cleaning impurities, etching, roughening and activation of the fiber surface. It could be made via bombarding fiber surface with high-energy particles such as free radicals, ions and electrons in the plasma stream [Adeniyi 2019, Oliveira 2019]. The plasma treatment can generate a variety of surface modification effects depending on the ionized gas type, exposure duration, microwave strength, and the distance of the fibers from the plasma source.

In atmospheric plasma systems, the overall plasma density is much higher causing the speed increase as well as the rate of incorporation of ionized molecules into the surface of the material. Thus, the fibers exhibit a higher surface energy. There are several types of plasma treatments, but low pressure plasma treatment is very often used for natural fiber surface treatment. This method is variable as several process gases or gas mixtures can be used, pressure and duration of action can be controlled. There is no mechanical effect when treating the fiber surface with low-pressure plasma and the thermal influence of the fiber surface is minimal [Gupta 2000].

In several publications, there had been evaluated enhancement of surface adhesion of natural fibers with PLA matrix, which after usage plasma surface treatment, evoked thermal stability, wettability and mechanical properties. In research of Jang et. al [Oliveira 2019], a positive effect of coconut fibers plasma treatment was detected on mechanical properties of PLA composites (increasing of tensile strength and Young´s modulus).

2 MATERIALS AND PROCESSING

The material designated Ingeo Biopolymer 3251D from NatureWorks LLC (USA) was selected to prepare the biocomposite. It concerns a biopolymer intended for processing via the injection technology and it is normally supplied as a granulate. The natural fiber was a coconut fiber obtained from the mesocarp layer. The fiber length ranged from 15 to 35 cm in the form of the raw material. Microscopic images of the coconut fibers are shown in Figure 1.

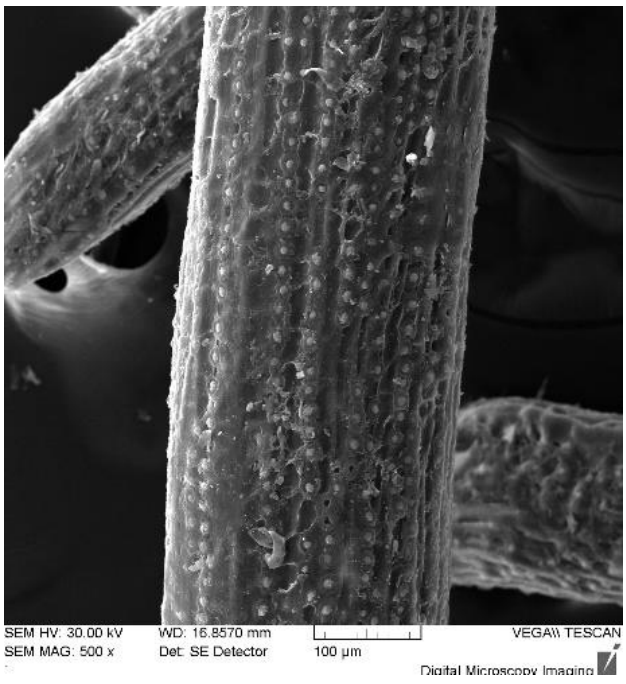

Figure 1. Microscopic image of coconut fibers (left) and fiber length distribution (right)

PLA dried in Maguire Low Pressure Dryer (LPD 100) under the following conditions: temperature 80 °C, time 180 min., Vacuum 0,8 bar to a residual moisture content of 0,025 %. The natural fibers were dried in the Venticell 222 hot air oven with forced air circulation at 80 °C for 180 min. prior to compounding. MSV Systems CZ equipment was used for plasma modification of coconut fibers, enabling low-temperature plasma technology consisting of two parallel electrodes covered with 1 mm dielectric layer between which a volumetric cold plasma discharge burned in filamentary mode. The electrodes were of rectangular size 50x60 mm with a thickness of 8 mm without active cooling and the distance between the electrodes was 15 mm. Plasma modification of coconut fibers (see Figure 2) had been carried out under the following conditions: voltage 20 kV, frequency 3 to 10 kHz, power 200 W.

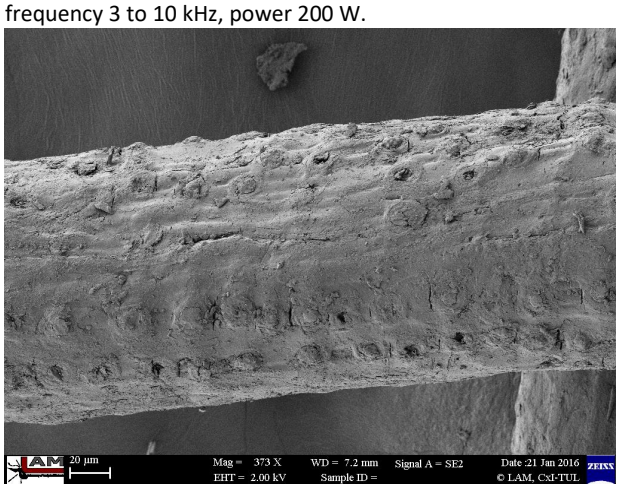

Figure 2. Microscopic image of coconut fibers after plasma modification, SEM

Biocomposite pellets were prepared by twin screw extruder (ZAMAK EHP-2x130di) followed by water bath and pelletizer. The temperature profile of extrusion line had been set from 140 °C up to 180 °C. Coconut natural fibers were directly dosed into the melting chamber of the extruder in the recommended front position by external device, working on the gravimetric principle. The reason for dosing at front parts of the extruder, is to prevent excessive shear stress of coconut fibers during melt compounding and thus prevent their damage or thermal degradation. Pelletized compounds passed through the water bath were dried before the injection molding at Maguire Low Pressure Dryer (LPD 100) under the following conditions: temperature 80 °C, time 180 min., vacuum 0,8 bar.

Three biocomposite materials with different percentages of natural fillers in the matrix (10, 20 and 30 %) with no plasma modification and plasma modification were compounded. Testing samples were injection molded according to ISO 527 and ISO 178 on the injection molding machine (ARBURG 270S 400-100) with the increasing temperature profile (165 °C up to 190 °C) of melting chamber and the injection rate of 35 cm3.s-1. Resulted biocomposites and control samples are shown in Table 1.

Sample code	Composition (wt%)		Plasma modification
	PLA	Coconut fibers	of fibers
PLA	100	-	-
PLA/10-CF	90	10	No
PLA/20-CF	80	20	No
PLA/30-CF	70	30	No
PLA/10-CF-PM	90	10	Yes
PLA/20-CF-PM	80	20	Yes
PLA/30-CF-PM	70	30	Yes

Table 1. PLA and biocomposite samples

3 METHODS

3.1 Unaxial tensile testing

For tensile testing of injection molded samples, Tiratest 2300 were used. Measurements were performed according to the STN EN ISO 527 standards with the tested samples gauge length of 80 mm. The samples were strained at the room temperature up to break at a test speed of 5 mm.min-1. The module of tensile elasticity was determined at a reduced test speed 1 mm.min-1. From the stress-strain dependences, tensile strength was calculated. The measurements were performed on 10 test samples at 23 °C. The average value and the standard deviation were calculated. The conditioning was carried out under the conditions according to STN EN ISO 291. LabNet was used for the evaluation.

3.2 Flexural testing

The flexural testing (according to STN EN ISO 178) was measured on a Hounsfield H10KT shredder. The conditioning was carried out according to STN EN ISO 291. Test samples of dimensions 80×10x4 mm were placed on two supports. To determine the modulus of elasticity, measurements were taken at a speed of 1 mm.min-1 with prestressing according to the standard. Measurements were performed on 10 specimens at 23 °C and the average value and the standard deviation had been calculated. The measured values were recorded by the Qmat program. It was necessary to determine the stresses (σ_{f2} and σ_{f1}) at a proportional elongation of 0,05 % (ε_{f1}) and 0,25 % (ε_{f2}), respectively. The modulus of elasticity itself was then calculated on the basis of formula 1

$$E_f = \frac{\sigma_{f2} - \sigma_{f1}}{\varepsilon_{f2} - \varepsilon_{f1}} \quad (1)$$

where E_f is the secant modulus [MPa], σ_{f2} is the elongation at 0,25 %, σ_{f1} is the elongation at 0,05 %, ε_{f2} is the elongation at 0,25 %, ε_{f1} is the elongation at 0,05 %.

3.3 Charpy impact

Charpy method was used for the determination of impact resistance according to STN EN ISO 179-1 on Resil 5.5. Prior to the measurement, the instrument was calibrated for mechanical resistance and air resistance at no load. Conditioning was carried out according to STN EN ISO 291. Test specimens had dimensions of 80×10x4 mm. Measurements were performed on 10 specimens at 23 °C and on 10 samples at -35 °C. After measurement, the impact strength a_{cU} was calculated according to the relationship 2 and the values were calculated as the average value and the standard deviation,

$$a_{cU} = \frac{E_c}{hb} \times 10^3 \quad (2)$$

where E_c the energy required to break the specimen [J] required is, h is the thickness of the specimen [mm], b is the width of the sample [mm].

3.4 Scanning electron microscopy (SEM)

Scanning electron microscopy was used to determine a fracture surface analysis in the central part of testing samples of bio-composites with natural fibers. The scanning electron microscope (SEM) had been conducted on Carl Zeiss ULTRA Plus (Carl Zeiss, Germany) at an acceleration voltage range of 2–5 kV.

3.5 Differential scanning calorimetry (DSC)

Non-isothermal study of crystallization was conducted by differential scanning calorimetry DSC 1/700 calorimeter (Mettler Toledo, Switzerland) according to ISO 11357. The instrument was calibrated via indium and zinc standard. About 5–8 mg of a sample was prepared from the cross-section of the test specimen on a rotating microtome Leica RM2255 (Leica Biosystem, Germany) for each formulation. The samples amount 10±1 mg were sealed in an aluminum pan and heated from 25 to 200 °C to remove previous thermal history and then cooled again. The second heating-cooling cycle analysis run at 10 °C min-1 heating/cooling ramp in a nitrogen atmosphere (flow rate 50 ml•min-1) to determine thermal transitions: glass transition (T_g), cold crystallization (T_{sc1} and T_{sc2}) and melting (T_m) temperatures and enthalpies (ΔH_{sc1}, ΔH_{sc2}, ΔH_m). The crystalline fraction X (%) of PLA-CF and PLA-CF-PM biocomposite samples was calculated based on the enthalpy value of a 100 % crystalline PLA (93 J.g-1) from the following equation:

$$X = \frac{(\Delta H_m - \Delta H_{sc1} - \Delta H_{sc2})}{(\Delta H_0 \cdot W_m)} \cdot 100\ [\%] \quad (3)$$

where X the degree of crystallinity is [%], ΔH_m is the change of melting enthalpy [J.g-1], ΔHsc1 is the enthalpy change of the 1st secondary crystallization [J.g-1], ΔHsc2 is the enthalpy change of the second secondary crystallization [J.g-1], ΔH_0 is the change of melting enthalpy 100% crystalline polymer [J.g-1], Wm is PLA matrix weight fraction in the biocomposite sample [-].

4 RESULTS AND DISCUSSION

Mechanical properties are summarized in Table 2. The table does not only show the effect of natural fibers on mechanical properties of biocomposites, but also the effect of plasma modification of the surface of natural fibers on mechanical properties, which are higher than those of biocomposites with natural fibers without any modification. From results can be concluded that the addition of coconut fibers increased the modulus of elasticity in tension. In contrast, the tensile stress decreases at the yield point with the addition of fibers. The relative elongation decreases at yield strength, when fibers are used. In flexural properties with increasing percentage of natural fibers, the flexural modulus increases.

Sample code	Tensile Modulus of Elasticity (1 mm.min^{-1}) [MPa] ISO 527/ 1B/1	Yield Strength (Ultimate Strength) (50 mm.min^{-1}) [MPa] ISO 527/ 1B/50	Nominal Strain at Fracture (50 mm.min^{-1}) [%] ISO 527/ 1B/50	Flexural Modulus (1 mm.min^{-1}) [MPa] ISO 178 1	Flexural Strength (1 mm.min^{-1}) [MPa] ISO 178 1
PLA	3394 ± 42	66.0 ± 1.1	2.3 ± 0.2	3168 ± 31	91.9 ± 1.5
PLA/10-CF	3614 ± 55	61.7 ± 0.7	2.0 ± 0.1	3366 ± 20	86.9 ± 0.8
PLA/20-CF	3852 ± 73	57.6 ± 0.5	1.8 ± 0.1	3474 ± 29	87.7 ± 0.8
PLA/30-CF	3975 ± 96	56.0 ± 0.6	1.6 ± 0.1	3618 ± 40	91.4 ± 1.0
PLA/10-CF-PM	4241 ± 64	66.2 ± 0.9	1.8 ± 0.1	4545 ± 45	93.0 ± 1.5
PLA/20-CF-PM	4542 ± 88	68.8 ± 0.9	1.7 ± 0.1	4680 ± 39	97.2 ± 1.8
PLA/30-CF-PM	4869 ± 83	71.6 ± 1.3	1.5 ± 0.1	4991 ± 61	96.3 ± 2.0

Table 2. Mechanical properties of PLA, PLA-CF and PLA-CF-PM biocomposites

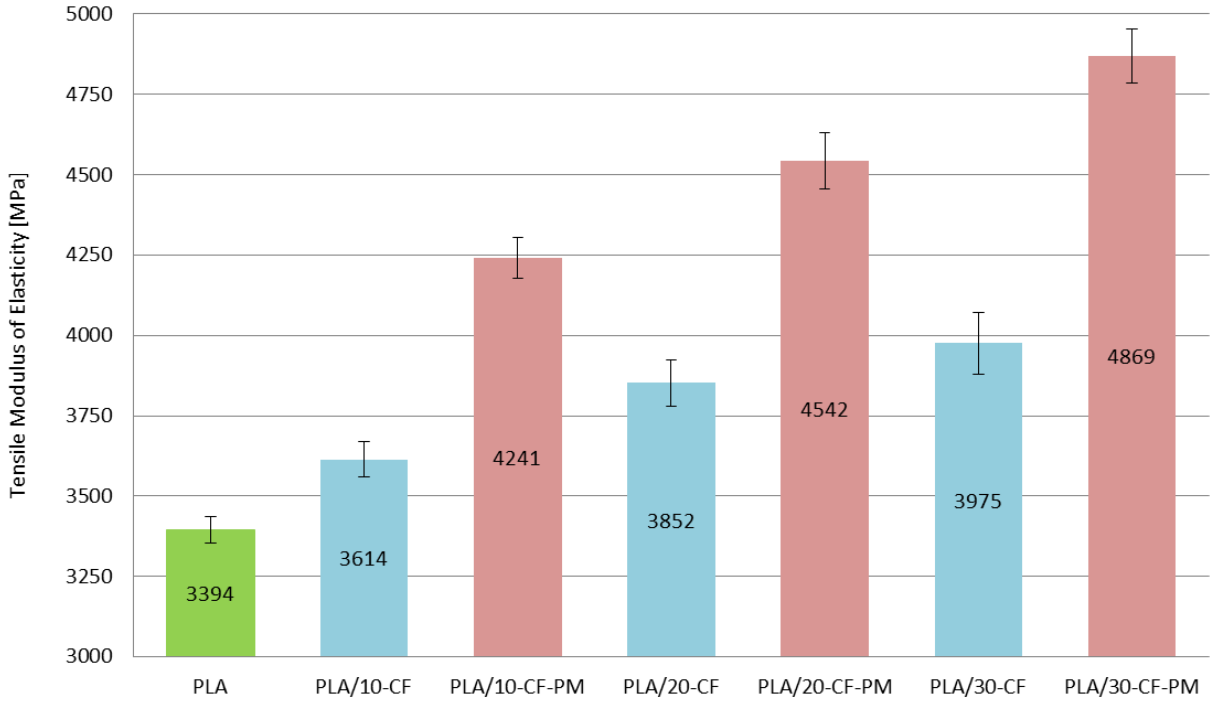

Figure 3. Modulus of Elasticity of PLA, PLA-CF and PLA-CF-PM biocomposites

The flexural modulus also increases thanks to plasma surface modification. The flexural tensile stress slightly increases with rising content of natural fibers. Tensile modulus of elasticity and flexural modulus are material characteristics, which are significantly influenced by the morphology and crystallinity of polymers. Especially, heterogeneous structure of surface layers is important for high values of modulus.

Table 2 does not only show the additive effect of natural fibers to the matrix of the PLA polymer, but mainly the effect of plasma coconut treatment on the tensile modulus of the PLA biocomposite, thanks to significantly better adhesion between the fiber and matrix at the biocomposite material interface (see Figure 6).

Compared to unfilled PLA, the tensile modulus increases of nearly 9 % for a 10 wt% of natural fibers without any modification, but with the modification leads to an increase by significant 25 % on the same percentage proportion. As the percentage proportion of natural fibers increases, even does increases the value itself too. For 20 wt% of natural fibers without any modification, there is an increase by 13 %, with plasma surface modification, it is even by 33 %. For 30 wt% of natural fibers, the tensile modulus values of a biocomposite are by 17 % higher without any surface modification and with the modification, they are higher by 43 %. From these values, it is apparent that the tensile modulus of unmodified natural fibers increases with each added 10 wt% of natural fibers in the biocomposite by about 4 %, but for plasma modified coconut fibers it is from 8 to 10 % (see Figure 3). The modulus of elasticity in tensile is about 20 % higher when comparing biocomposites with unmodified and modified natural fibers by applying plasma surface modification.

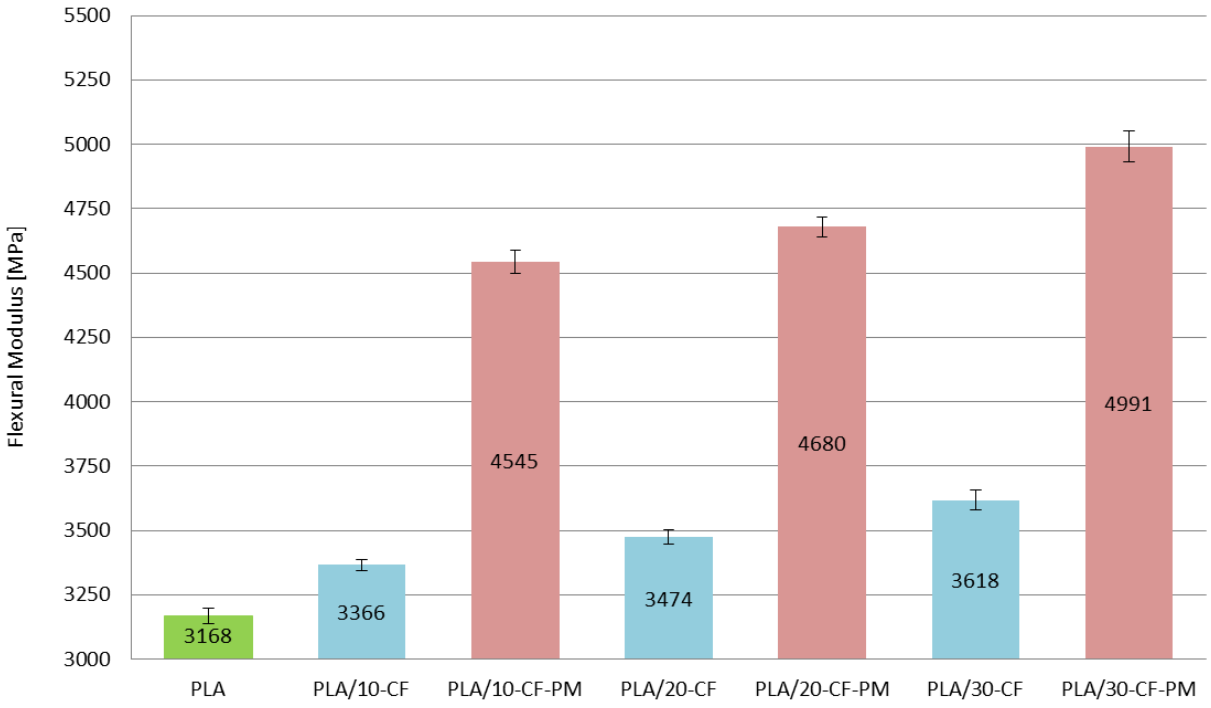

Figure 4. Flexural Modulus of PLA, PLA-CF and PLA-CF-PM biocomposites

Yield Strength (Ultimate Strength) results show that biocomposites with plasma modified natural fibers exhibit an increase in yield stress with an increasing fiber content in the PLA matrix, which is in the order of percentage units. Conversely, for biocomposites with untreated fibers when increasing fiber content, the yield strength decreases, by about 5 % for every 10 wt% natural fibers. The relative elongation at yield of the PLA matrix of Ingeo biopolymer 3251D is very low (2,3 %) and decreases with the addition of natural fibers: both for the surface modified as well as unmodified coconut fibers.

By the addition of fibers, the flexural modulus increases as well as the tensile modulus. Values obtained from measurements shown in the Table 2, do not only confirm the increase in flexural modulus with the rising of coconut fiber percentage, but especially, the extraordinary efficiency of the plasma surface treatment of fibers. This significant increase has been caused by significantly better adhesion between the fiber and the matrix at the interfacial interface of the biocomposite material. This is identified thanks to the application plasma modification of the coconut fiber surface (see Figure 6). When using 10 wt% of coconut fibers without any modification, the increase in flexural modulus versus PLA is about 6 %, at 20 wt%, the flexural modulus increase is by 9 % and for 30 wt%, it is around 14 %. When a plasma modification of the coconut fiber surface is applied, the flexural modulus increase is 43 %, 47 %, respectively, 57 % over PLA. From these values, it is apparent that the flexural modulus of unmodified natural fibers increases with each added 10 wt% of natural fibers in the biocomposite by about 4 %, but for plasma modified coconut fibers it is about 7 % (see Figure 4). Plasma treatment of fiber surfaces caused an increase in flexural modulus by more than 35 % for biocomposites compared to biocomposites without the surface modification of natural fibers for all percentages, which is roughly twice as much as than it had been achieved with the tensile modulus.

The flexural strength of the coconut fiber biocomposite exhibits similar dependencies to the tensile yield stress. For a biocomposite with untreated fibers, the values obtained are always lower than those of unfilled PLA and, with increasing natural fiber content, the flexural strength limit increases by several percent. In biocomposite with plasma-coated fibers, there is the ultimate flexural strength higher than the value for PLA, and the stress increases in the order of percent units with rising percentage proportion of natural fibers in the matrix.

Impact toughness measurements were performed for temperature +23 ° C. Impact toughness results at both temperatures are shown in the Table 3 indicating a decrease in toughness in biocomposites when a fibrous filler applied. The impact toughness of the PLA matrix is relatively low and the addition of coconut fibers always causes a decrease of this mechanical property. According to results of the impact strength measurements at +23 ^{o}C demonstrated in the Table 3, a gradual loss of toughness is evident with the increasing addition of coconut fibers. As a result of a plasma surface treatment, the impact resistance is further reduced by average additional of 5 %. Overall impact reduction of PLA biocomposite with the addition of plasma treated coconut fibers 10, 20 and 30 wt% relative to the PLA matrix amounts to 28,3 %, 33,5 %, or more precisely, 32,7 %.

Sample code	Impact strength Charpy 23 °C [kJ.m^{-2}] ISO 179-1/1eU
PLA	25.1 ± 2.5
PLA/10-CF	19.1 ± 0.9
PLA/20-CF	18.2 ± 1.0
PLA/30-CF	17.0 ± 1.3
PLA/10-CF-PM	18.0 ± 1.3
PLA/20-CF-PM	16.7 ± 1.6
PLA/30-CF-PM	16.9 ± 1.4

Table 3. Charpy impact properties of PLA, PLA-CF and PLA-CF-PM biocomposites

Due to its slow crystallization rate, PLA is characteristic in heating phase with cold crystallization and sometimes also with pre-melt crystallization. The level of these exothermal reactions has an influence on values heat of crystal melting. Consequently, the values of heat of cold and pre-melt crystallization is necessary to subtract from the heat of melting of PLA, or more precisely, PLA composites. Differential scanning calorimetry was used to investigate the effect of coconut fibers content on the glass transition, non-isothermal crystallization and melting phenomena of biocomposites. Resulted thermal properties are summarized in the Table 4. Secondary crystallization occurred in all investigated biocomposites. A region of the first secondary crystallizations lies between (79 ÷ 122) °C and the region of the second secondary crystallizations lies between (150 ÷ 161) °C and 60 °C, or more precisely below the lower melting point of biocomposites. At the end of the second phase of secondary crystallizations, the melting of materials occurs having a peak at about 171 °C. This phase ends at a temperature of approximately 185 °C. Values of the first secondary crystallization decrease with an increasing weight fraction of coconut fibers. Regarding the region of the second secondary crystallization, values increase with the rising coconut fiber weight fraction. Plasma treated coconut fiber behaves similarly in biocomposite systems (there is a decrease in enthalpy in the first secondary crystallization in comparison with PLA polymer and an increase in the second secondary crystallization), but the percentage changes are higher. Values of the first secondary crystallization decrease with an increasing weight fraction of coconut fibers. Size ΔH_{sc1} for PLA biocomposite with 10 wt% of coconut fibers is dropping to 26,3 J.g-1 representing a decrease of less than 11 % compared to PLA biopolymer. For PLA composite with 30 wt% of coconut fibers it is dropping to 3 J.g-1, representing a decrease of less than 25 %. For the region of the second secondary crystallization, the value ΔH_{sc2} is the difference almost 56 % between the PLA polymer and the 30 wt% biocomposite of coconut fiber. Plasma processed coconut fiber behaves similarly in biocomposite systems, however the percentage changes are higher. For a 10 wt% of the plasma modified fibers, there is about 14 % of decrease in enthalpy in the first secondary crystallization compared to PLA polymer. For a composite with 30 wt% plasma processed fibers, the decrease is nearly 55 %. Magnitude of the change in enthalpy conversion of the second secondary crystallization (ΔH_{sc2}) did not change for a 10 wt%. In the case of a composite with 30 wt% of plasma treated fibers, the ΔHsc2 value increased by almost 78 % in comparison with the polymer PLA.

From the point of view of polymer morphology, a degree of crystallinity X is very important. The degree of crystallinity of a biocomposite with 10 wt% of coconut fiber increased by 30 % compared to pure PLA, for biocomposite with 20 wt% of the fibers increased by almost 48 % and the biocomposite with 30 wt% of the fibers increased by 62 %. For the biocomposite with plasma-treated fibers, the increases in the degree of crystallinity were similar, i.e. 30 %, 53 %, or more precisely 70 %. An important aspect of the fibrous filler composites is the size and quality of the interfacial adhesion between fibers and the polymer matrix. The degree of interfacial adhesion is a decisive factor in the utilization of the reinforcing fiber potential. To evaluate the interfacial adhesion at the interface of plant fibers and PLA biopolymer matrix, SEM images of fracture surfaces of PLA biocomposites with coconut fibers without surface modification and plasma surface modification were taken. Figure 5 (down) shows images of fracture surfaces of co-injected PLA biocomposites without surface modification. These images show a very low adhesion between the fiber and the polymer matrix. The fibers are not encapsulated by the PLA matrix, and their cohesion with the matrix is influenced only by the geometric bond.

Sample code	ΔC_p [J·g^{-1}·K^{-1}]	T_g [°C]	T_m [°C]	ΔH_{sc1} [J·g^{-1}]	ΔH_{sc2} [J·g^{-1}]	ΔH_m [J·g^{-1}]	χ [%]
PLA	0.73	61.0	170.7	29.6	0.9	38.9	9.0
PLA/10-CF	0.47	61.6	171.8	26.3	1.0	37.1	11.7
PLA/20-CF	0.53	63.0	172.0	24.5	1.3	35.7	13.3
PLA/30-CF	0.55	60.8	171.5	22.3	1.4	33.2	14.6
PLA/10-CF-PM	0.50	60.9	171.6	25.2	0.8	35.8	11.7
PLA/20-CF-PM	0.47	61.5	171.4	20.0	1.5	31.8	13.8
PLA/30-CF-PM	0.45	61.3	171.0	13.4	1.6	25.0	15.3

Table 4. Thermal properties from DSC analysis of PLA, PLA-CF and PLA-CF-PM biocomposites

The images show cavities in the PLA matrix due to the extraction of coconut fibers during loading. This fact fully corresponds with the measured values of mechanical properties of biocomposites. Fracture images of coconut fiber PLA biocomposites whose surface has been plasma modified are shown in the Figure 5 (up). The images show a significant improvement in interfacial adhesion. The interface has improved between fiber and matrix interfaces has improved and also does not pull the fibers out of the matrix, but breaks the fibers during stress; to break the fibers during stress.

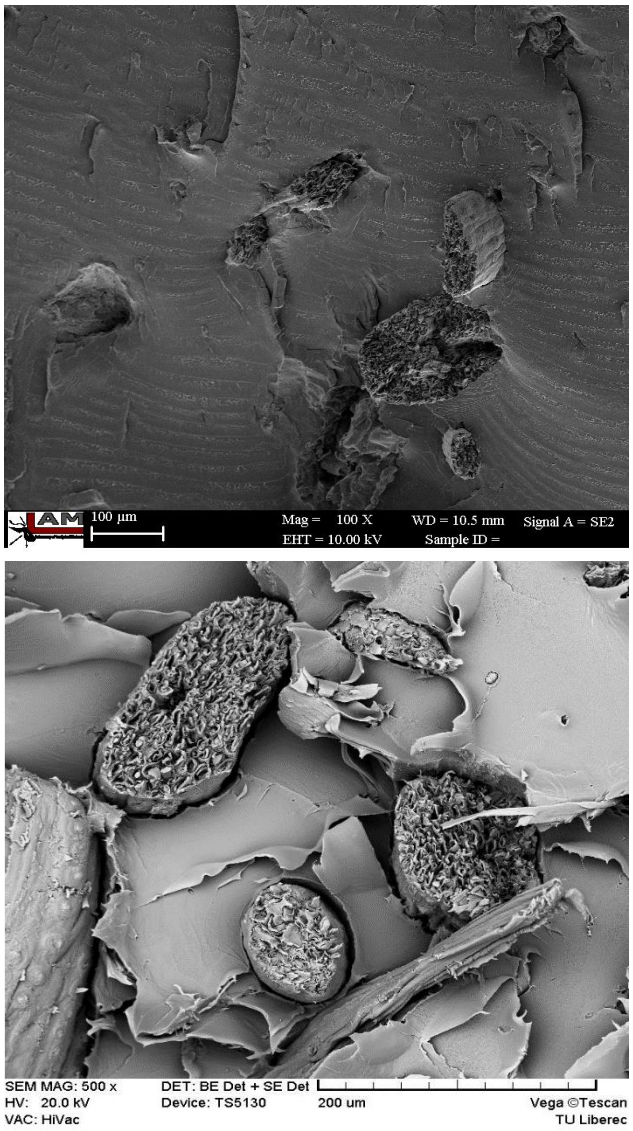

Figure 5. Microscopic images of fracture surfaces of PLA bio composite with coconut fibers without plasma surface treatment (down) and with plasma surface modification (up), SEM

5 CONCLUSIONS

Recently, biocomposite materials have become the focus of an interest and a wide range of research activities, material manufacturers, processors and final users. Biocomposite materials based on PLA matrices and plant fibers have great prerequisites for a wide application, as mentioned in Chapter 1

From the experimental results, the following conclusions can be drawn:

- The application of coconut fibers to PLA increases the modulus of elasticity as well as flexural modulus, and these modules have further risen with increasing percentages of the fiber. The tensile and flexural modulus of unmodified natural fibers increases with each added 10 wt% of natural fibers in the biocomposite by about 4 %.
- The application of coconut fibers to PLA increases the modulus of elasticity as well as flexural modulus These modules have further risen with increasing percentages of the fiber. The tensile and flexural modulus of unmodified natural fibers increases with each added 10 wt% of natural fibers in the biocomposite by about 4 %.
- The application of the plasma modification of the surface of natural fibers led to an increase in the values of the modulus of elasticity in tension and bending compared to the biocomposites with natural fibers without modification. The modulus of elasticity increases with each added 10 wt% for plasma-modified coconut fibers by 8 to 10 % and a flexural modulus of about 7 %.
- The modulus of elasticity is about 20 % higher in tensile comparing biocomposites with unmodified and modified natural fibers when applying a plasma surface modification.
- The flexural modulus when compared to biocomposites with unmodified and modified natural fibers is more than 35 % higher than biocomposites without a surface modification of natural fibers for all percentages, which is roughly twice the increase in the tensile modulus.
- Addition of coconut fibers reduced the tensile yield stress by about 5 % for every 10 wt% natural fibers. For biocomposites with plasma modified natural fibers, the yield stress increases with an increase in the fiber content in the PLA matrix, which is in the order of one percent. The relative elongation at yield strength decreases with the addition of natural fibers, both for surface-modified and unmodified coconut fibers.
- The flexural stress is increasing slightly with an increasing content of unmodified natural fibers. In a biocomposite with plasma-coated fibers, the ultimate flexural strength increases by several percent as the percentage of natural fibers in the matrix increases too.
- The impact toughness results show a decrease in the toughness of biocomposites when the fibrous filler is applied to the PLA polymer at both temperatures with an increasing percentage of coconut fibers. Due to the plasma surface treatment, the impact resistance is further reduced by an additional 5 % on average. A higher decrease was achieved by impact toughness at positive temperatures (decrease of impact toughness of PLA biocomposite with the addition of plasma modified coconut fibers 10, 20 and 30 wt% compared to PLA matrix is 28,3 %, 33,5 % and 32,7 % for temperature 23 ^{o}C.
- A significant first and the second secondary crystallization was detected by DSC method. Values of the first secondary crystallization decrease with an increasing weight proportion of coconut fibers. Plasma modified surface of coconut fibers behaves similarly in biocomposite systems, but the percentage changes are higher. From the calculated degrees of crystallinity, the positive influence of coconut fibers is evident on the morphology, where the proportion of crystalline phase increases with an increasing fiber addition. Plasma treated fibers exhibit only a slightly higher degree of crystallinity of the biocomposite. The degree of crystallinity of a biocomposite with 10 wt% of coconut fiber increased by 30 % compared to pure PLA, for biocomposite with 20 wt% of the fibers increased by almost 48 %, or more precisely 53 % for plasma treated fibers

and biocomposite with 30 wt% of the fibers increased by 62 %, or more precisely by 70 %.

Experimental results of mechanical properties confirmed that by using plasma treatment of natural coconut fibers by means of DBD technology (low-temperature plasma - atmospheric barrier discharge), the final properties of biocomposites with PLA matrix can be positively influenced by previously performed experiments by Faruk [Faruk 2011], Mohanty [Mohanty 2005] and Plackett [Plackett 2005]. Surface modification of natural fibers by plasma is an ecological alternative to other types of treatments, e.g chemical one, which allows preparation of completely natural biocomposite materials only from renewable sources without chemical additives.

ACKNOWLEDGMENTS

This work was supported by the Ministry of Education, Youth and Sports of the Czech Republic and the European Union - European Structural and Investment Funds in the frames of Operational Program Research, Development and Education - project Hybrid Materials for Hierarchical Structures (HyHi, Reg. No. CZ.02.1.01/0.0/0.0/16_019/0000843).

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