

THERMAL AND MECHANICAL PROPERTIES OF BIOCOMPOSITES BASED ON GREEN PE-HD AND HEMP FIBERS

Silvester Bolka^{1*}, *Janez Slapnik*¹, *Rebeka Rudolf*², *Rajko Bobovnik*¹, *Maja Mešl*¹

¹ Polymer Technology College, Ozare 19, 2380 Slovenj Gradec, Slovenia

² University of Maribor, Faculty of Mechanical Engineering, Smetanova 17,
2000 Maribor, Slovenia

Summary: Biocomposites of hemp fiber reinforced bio-based high density polyethylene (green PE-HD) were prepared using a maleic anhydride grafted styrene–ethylene/butylene–styrene (SEBS-*g*-MA) as a compatibilizer. Several compositions of biocomposites were prepared on a twin screw extruder using the full factorial design varying two factors with two levels. The mechanical and thermal properties of test specimens, prepared by injection molding, were investigated by tensile and bending tests, DMA, and ultra-fast differential dynamic calorimetry (Flash DSC). High stiffness and strength of biocomposites in comparison to neat green PE-HD indicate very good compatibility of the constituents. Stiffness of the samples without SEBS-*g*-MA is slightly higher than that of the samples with SEBS-*g*-MA. The thermal stability of biocomposites is for all samples drastically higher as compared to neat green PE-HD. The melting (T_m) and crystallization (T_c) temperatures of the biocomposites are shifted to higher temperatures. Incorporation of SEBS-*g*-MA together with hemp fiber into the matrix enhances strength, stiffness, impact strength and rises thermal stability. The novel biocomposites are suitable for applications such as technical parts, which require higher stiffness and thermal stability as compared to neat green PE-HD.

Keywords: high density polyethylene (PE-HD), hemp fiber, maleic anhydride grafted styrene–ethylene/butylene–styrene (SEBS-*g*-MA), characterization.

1. INTRODUCTION

A composite is composed of two or more physically distinct phases whose combination produces mechanical-properties that are different from those of its constituents. Polymer composites are very important because of remarkable strength and stiffness, yet very light in weight. The ratios of strength to weight and stiffness to weight are several times stronger than those of steel or aluminum and it is also possible to achieve combinations of properties not attainable with metals, ceramics, or polymers alone [1]. Natural fibers have recently become attractive to researchers, engineers and scientists as an alternative reinforcement for glass fiber composites. Due to their low cost, fairly good mechanical properties, high specific strength, non-abrasive and eco-friendly characteristics, they are exploited as a replacement for the conventional fibers, such as glass and carbon. The tensile properties of natural fibers reinforced polymers (both thermoplastics and thermosets) are mainly influenced by the interfacial

adhesion between the matrix and the fibers. A chemical modification or the addition of compatibilizers and dispersing agents are needed to improve the interfacial matrix-fibers bonding resulting in the enhancement of mechanical properties of the composites. Although grafting onto fibers surfaces can improve the properties of the composites to a significant extent, this process increases the material cost. The use of specific interfacial additives, dispersing agents or compatibilizers is a cheaper route to improve properties and makes more practical sense for high volume, low cost polymer composite. In general, the tensile strengths of the natural fibers reinforced polymer composites increase with fiber content, up to a maximum or optimum value. However, the Young's modulus (E modulus) of the natural fiber reinforced polymer composites increases with increasing fiber loading [1–4]. The longitudinal E modulus can be calculated according Halpin-Tsai semi-empirical relation by rule of mixtures using strength of materials approach:

$$E = E_F V_F + E_M V_M \quad (1)$$

* Corresponding author: email: silvester.bolka@vstp.si

where E_F , E_M and V_F , V_M are the moduli and volume fractions of the fiber and matrix respectively [5].

Melt blending of a compatibilizer (polyethylene-grafted maleic anhydride, PE-g-MA) for the high-density polyethylene and natural fibers composite enhanced its mechanical strength. At 30 wt.% fiber loading, the tensile strength and tensile modulus decreased due to the increase in the interfacial adhesion between the fibers and matrix [6]. PE-g-MA enhanced tensile, flexural and impact strength in the HD-PE/jute composites. With the addition of 1 wt.% of PE-g-MA, the increase in strengths was reported: for tensile strength 47.3%, flexural strength 26.4% and impact strength 28.1% [7]. In the bentonite filled polypropylene composite, the addition of the polypropylene grafted-maleic anhydride (PP-g-MA) resulted in enhanced mechanical and thermal properties. SEM morphological investigation showed the improvement in thermal stability, reduced water absorption, higher impact strength and elongation at break due to improved interfacial adhesion between filler and matrix [8]. Maleic anhydride can be also used for coating of fibers to reduce their hydrophilicity [9–11].

The best distribution of wood flakes and fibers in the HD-PE can be achieved by compounding them on a twin-screw extruder. With this mixing technique, the best wettability and acceptable mechanical properties can be achieved [12].

The primary drawback of the use of natural fibers is the lower processing temperature due to the possibility of natural fibers degradation. The processing temperatures are thus limited to about 200°C, although it is also possible to use higher temperatures, but only for short periods. This limits the type of thermoplastics that can be used with agro-fibers to commodity thermoplastics such as polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC) and polystyrene (PS). The second drawback is the high moisture absorption of the natural fibers. Moisture absorption can result in swelling of the fibers and concerns on the dimension stability of the agro-fiber composites cannot be ignored. However, the absorption of moisture by the fibers in the composite is minimized due to encapsulation by the polymer. Nevertheless, it is difficult to entirely eliminate the absorption of moisture on the composite surface without using expensive surface barriers. If necessary, the moisture absorption of the fibers can be dramatically reduced through chemical modification of some of the hydroxyl groups present in the fiber [Rowell et al. 1986] but with some increase in the cost of the fiber. Good fiber-matrix bonding can also reduce the rate and amount of water absorbed by the composite [13].

In the present study, a systematic investigation was conducted on the effects of loading of the hemp fiber and compatibilizer maleic anhydride grafted styrene-ethylene/butylene-styrene (SEBS-g-MA) to obtain the optimal thermal, mechanical and morphological properties of the green-PE-HD biocomposites. The composites were prepared through melt blending process on a twin-screw extruder and test specimens by injection molding. The general objective of this study was to investigate the potential of the usage of green PE-HD biocomposites as technical parts with enhanced strength, stiffness and thermal stability.

2. MATERIALS AND METHODS

2.1. Materials for composite

Commercially available polyethylene high density grade green HDPE SHC 7260 was purchased from Braskem (delivered by Resinex, Slovenia). It is injection molding grade with high stiffness and strength, with minimum 94 wt% renewable resources ingredients (from sugarcane). The melt flow rate (according to ASTM D 1238 at 190 °C with 2.16 kg) is 7.2 g/10 min., density (according to ASTM D 1505/D 792) 0.959 g/cm³ and deflection temperature under load (according to ASTM D 648 with 0.45 MPa) 76 °C. The hemp was delivered as the sample in the form of stems of the industrial hemp from farmer cooperative Zadruga Konopko from Slovenia. Commercially available compatibilizer SEBS-g-MA (maleic anhydride grafted styrene-ethylene/butylene-styrene) was purchased from Auserpolimeri, Italy.

2.2. Preparation of the material

The pretreatment of the matrix and compatibilizer was not necessary. The stems of the industrial hemp were cryogenically grinded for 10 min. to the length of approximately less than 2 mm. For the determination of the influence of the added compatibilizer and hemp fiber, it was decided to make full factorial design (design of experiments) varying two factors with two levels as shown in the Table 1. The addition of hemp was 2 wt. % and 10 wt. %, the addition of SEBS-g-MA was 0 wt. % and 2 wt. %. In addition to four compositions, the central point experiment was carried out as a control as well as the neat green PE-HD as a reference. The matrix and the compatibilizer were in pellet form, the hemp in fiber form. For all runs, the materials were separately mixed together and extruded on the double screw extruder Labtech LTE 20-44. The screws diameters were 20 mm, L/D ratio 44:1, screws rotation

150 rpm, temperature profile was increasing from the hopper (130 °C) to the die (155 °C). The temperatures were set as low as possible to prevent hemp fibers thermal degradation during extrusion. [14] The composite material was extruded through the die with two circular holes with the diameter of

3 mm. After extrusion the two filaments were cooled in the water bath with the temperature of 25 °C and granulated on Scheer granulator into the approximate dimensions of 3 mm for diameter and 4 mm for length.

Table 1. Composition of biocomposites for the extrusion

Sample	SHC 7260 [wt. %]	Hemp fibers [wt. %]	SEBS-g-MA [wt. %]
1	98	2	0
2	90	10	0
3*	93	6	1
4	96	2	2
5	88	10	2
6	100	0	0

* - central point (mid values of parameters)

2.3. Injection molding

Due to water bath cooling of the material after extrusion, the pellets were dried to the humidity of max. 0,03% at 80 °C for 4 hours. The injection molding was performed on Krauss Maffei 50-180 CX injection molding machine with the screw diameter of 30 mm and clamping force of 500 kN. For the sample production, the cold runner was used, the tool had two cavities, one with the dumbbell-shaped type 1BA shape (ISO 527-1), the second with cuboid shape (ISO 178/ISO 179). The temperature profile was increasing from the hopper (165 °C) to the die (185 °C), injection speed was set to 75 mm/min, at plasticizing the back pressure was set to 50 bars and screw rotation to the 50 rpm. The tool temperature was set to 50 °C and the cooling time to 25 s [15].

2.4. Characterization

ATR FT-IR spectra were recorded on a Perkin Elmer Spectrum 65 FT-IR spectrometer equipped with an ATR upgrade (Universal Accessory with Diamond ATR Top-plate - ZnSe) with a spectral resolution of 4 cm⁻¹ and a measuring range from 600 cm⁻¹ to 4000 cm⁻¹. For the evaluation of the results, the Spectrum software, Version 10.03.09.0139, was used.

Thermo-mechanical properties were examined using a Perkin Elmer DMA 8000 [16] dynamic mechanical analyzer. For the evaluation of results, the TT_DMA software, Version 14310, was used. The viscoelastic properties of the samples were analyzed by recording the storage modulus (E'), loss modulus (E'') and loss factor (tan δ) as a function of temperature. For the analyses of test samples, the DMA instrument was operated in the dual cantilever mode. The viscoelastic analyses were carried out on samples

with dimensions of approximately 42 x 5 x 2 mm. The samples were heated at 2 °C/min from room temperature to 180 °C under air atmosphere. A frequency of 10 Hz and amplitude of 20 μm were used [14].

Thermogravimetric analyses (TGA) were performed on a Perkin Elmer TGA 4000 thermal analysis instrument. For the evaluation of results, the Pyris software, Version 10.02.0468, was used. The analyses were carried out in a nitrogen atmosphere from 40 to 900 °C with a heating rate of 10 °C/min using an Al₂O₃ crucible without a lid [14].

Flexural tests were conducted according to ISO 178 on the Shimadzu AG-X plus [16] equipped with a load cell of maximum 10 kN, at a crosshead speed of 2 mm/min and span width of 64 mm. For the evaluation of the results, the TrapeziumX software, Version 1.3.1, was used. The samples were injection molded according to ISO 178 with the dimensions 80 x 10 x 4 mm. Five replicates for each sample were tested. All tests were performed at 23 °C.

Tension tests were conducted according to ISO 527-1 on the Shimadzu AG-X plus [16] equipped with a load cell of maximum 10 kN, at a crosshead speed of 1 mm/min to the extension of 0,25%, following with 50 mm/min to the break, with the strain measured in the mid-span of each specimen with an optical extensometer Shimadzu TRViewX. For the evaluation of the results, the TrapeziumX software, Version 1.3.1, was used. The samples were injection molded according to ISO 527-2, on dumbbell-shaped specimens type 1BA. Five replicates for each sample were tested. All tests were performed at 23 °C.

For the ultrafast scanning DSC measurements, the Mettler Toledo Flash DSC 1 calorimeter [17, 18] was used. For the evaluation of results, the Star^c

software, Version 12.10, was used. The samples were placed directly onto the sensitive area of the chip sensor with the diameter 0.5 mm. The sample mass must be from 10 ng to 1,000 ng, so that the ultrafast heating and cooling rates can be achieved; the heating rates are from 1 K/s to 40,000 K/s and the cooling rates from -1 K/s to -4,000 K/s. Fast scanning calorimeter was calibrated using melting temperature of metal indium and the experiments were done at ambient pressure. Nitrogen was used as purge gas (50 ml/min). The Flash DSC 1 was connected to the IntraCooler Huber TC 45. For the measurements, the temperature of the sensor support was set to 15 °C to prevent dewing of the sensor and sensor support metal plate. The samples were heated with 1,000 K/s from 15 °C to 220 °C, kept at this temperature for 0,1 s in order to erase thermal history and then cooled to 15 °C with the cooling rates from 1 K/s to 1,000 K/s. For the determination of the crystallization half-time, the isothermal method for the period of 2 s at the temperatures 117, 118 and 119 °C were used [14].

Impact tests were performed on the pendulum Zwick [16, 19] impact testing machine. The samples were injection molded according to ISO 179, notched and un-notched, with the dimensions 80 x 10 x 4 mm.

The morphologies of the contact surfaces between the hemp fiber and green PE-HD matrix were investigated using a Jeol scanning electron microscope. The surface of bulk samples was examined, freeze-fractured in liquid nitrogen. The samples were sputter-coated with a fine layer of gold in a sputter coater and analyzed [16].

3. RESULTS AND DISCUSSION

3.1. ATR FT-IR analysis

Frequency range at 2913 cm^{-1} ($-\text{CH}_2$ asymmetric stretching) is shifted to the higher frequencies. For 0,2 cm^{-1} for 2 wt.% addition of hemp fibers and for 0,6 cm^{-1} for 10 wt. % addition of hemp fibers. For the samples of biocomposites with SEBS-g-MA is the shift of this peak to the lower wave number comparing to the biocomposites without SEBS-g-MA and also compared to neat matrix. Frequency range at 2846 cm^{-1} ($-\text{CH}_2$ symmetric stretching) is shifted to the higher frequencies with the addition of 10 wt. % of hemp fiber (+0,5 cm^{-1}). With the addition of SEBS-g-MA, the phenomena are like at the asymmetric stretching - the peak is shifted to the lower wave number comparing to the biocomposites without SEBS-g-MA and also compared to neat matrix. (Table 2) Those results show bad interaction between matrix and hemp fibers, without SEBS-g-MA. Shift to the higher frequencies indicates higher crystallinity of polyethylene. We can assume, that hemp fibers acts as nuclei for the heterogenic crystallization behavior of polyethylene. This assumption was confirmed later on with Flash DSC measurements. With addition of SEBS-g-MA, the peaks are shifted to the lower wave numbers indicating better interactions between matrix and hemp fibers. Also this assumption was later on confirmed with TGA, DMA bending and tensile tests results and on the end also with the SEM analysis of fracture surfaces.

Table 2. Asymmetric (2913 cm^{-1}) and symmetric (2846 cm^{-1}) stretching of green PE-HD/hemp fibers/SEBS-g-MA biocomposites

Sample	Wavenumber [cm^{-1}]	Wavenumber [cm^{-1}]
1	2913.0	2846.0
2	2913.4	2846.5
3	2912.4	2845.4
4	2912.8	2845.8
5	2912.5	2845.7
6	2912.8	2846.0

3.2. Dynamical mechanical analysis

The addition of hemp fibers increases the storage modulus (E') at 30 °C as well as 100 °C whereas the addition of SEBS-g-MA lowers E' . Loss factor ($\tan \delta$) is reduced by the addition of hemp fibers and increased with the addition of SEBS-g-MA. The highest E' at 30 °C (1,817 MPa) and at 100 °C (412 MPa) was measured for the sample with 10 wt. % hemp fibers. The increase of stiffness regarding the neat green PE-HD

was 65% at 30 °C and 178 % at 100 °C. The highest loss factor was determined for neat matrix and the lowest for the sample with 10 wt.% hemp fibers. It can be concluded, that the addition of hemp fibers into the green PE-HD matrix rises the stiffness and the temperature resistance of the biocomposites. The addition of SEBS-g-MA into the green PE-HD matrix reduces the stiffness and temperature resistance of the biocomposites (Figure 1). With the addition of SEBS-g-MA, the biocomposites show better damping performance than

neat PE-HD. It has already been found that fine dispersed SEBS-g-MA domains increase interfacial interac-

tion between hemp fibers in the green PE-HD matrix in the ternary blends [15].

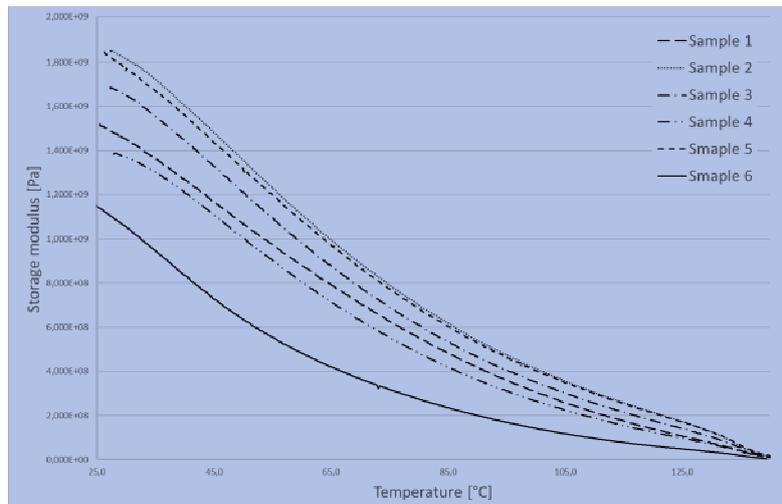


Figure 1. Storage modulus of the samples 1-6 (for designation see Table 1).

3.3. Thermogravimetric analysis

All biocomposites samples showed two-step thermal degradation process. The first degradation step at the temperatures from 362 °C to 374 °C (T_{d1}) is due to the thermal degradation of hemp fibers, while the second degradation step at the temperatures from 487 °C to 494 °C (T_{d2}) is due to the thermal degradation of the green PE-HD and SEBS-g-MA. The degradation temperature of the green PE-HD for the biocomposites without compatibilizer is decreased, which is more pronounced for the small amount of hemp fibers. The degradation temperature of the hemp fiber is the lowest for the biocomposites with 2 wt. % hemp fibers (samples 2 and 4). By addition of SEBS-g-MA into the biocomposites with 2 wt.% hemp fibers (sample 4), the thermal degradation temperature of hemp fibers rises from 362 °C to 374 °C, while the thermal degradation temperature of the matrix reduces from 492 °C to 487 °C in comparison with biocomposites without SEBS-g-MA. The thermal degradation temperature of hemp fibers in the biocomposite with 2 wt. % SEBS-g-MA and 10 wt.% hemp fibers (sample 5) rises to 365 °C and the thermal degradation temperature of matrix also rises to 492 °C in comparison with biocomposites without SEBS-g-MA. The thermal degradation temperature of the matrix of the biocomposites with 10 wt.% of hemp fibers and 2 wt.% SEBS-g-MA is the same in comparison with neat green PE-HD. (Table 3). The highest thermal degradation temperature of hemp fibers has the biocomposite with 2 wt.% hemp fibers and 2 wt.% SEBS-g-MA, the highest thermal degradation temperature of the matrix has the biocomposi-

te with 5 wt.% hemp fibers and 1 wt.% SEBS-g-MA. The conclusion could be that the addition of SEBS-g-MA increases the thermal degradation temperature of the hemp fibers due to better interactions between fibers and thermoplastic matrix, which is also supported by ATR FT-IR measurements.

Table 3. Thermal degradation of green PE-HD/hemp fibers/SEBS-g-MA biocomposites

Sample	T_{d1} [°C]	T_{d2} [°C]
1	362.0	490.0
2	362.8	490.8
3	367.6	494.2
4	374.4	487.3
5	365.4	491.8
6	/	491.8

3.4. Flexural properties

The addition of hemp fibers rises the stiffness and bending strength of the biocomposites but, at the same time, also reduces the yield strain. The addition of the SEBS-g-MA to green PE-HD/hemp fiber biocomposites reduces stiffness and bending strength, but rises the yield strain of the biocomposites. The highest E modulus and bending strength was determined for the biocomposite with 10 wt.% hemp fibers and without SEBS-g-MA, while the neat green PE-HD had the highest yield strain. (Figures 2-4) At bending tests, the addition of SEBS-g-MA reduces the stiffness and strength of the biocomposites due to low compressive stiffness and strength of SEBS-g-MA and perpendicular orientation of hemp fibers due to large thickness of injec-

tion molded samples. SEBS-g-MA acts as an effective compatibilizer, as indicated by higher yield strain of the biocomposites with SEBS-g-MA in

comparison to the biocomposites without compatibilizer.

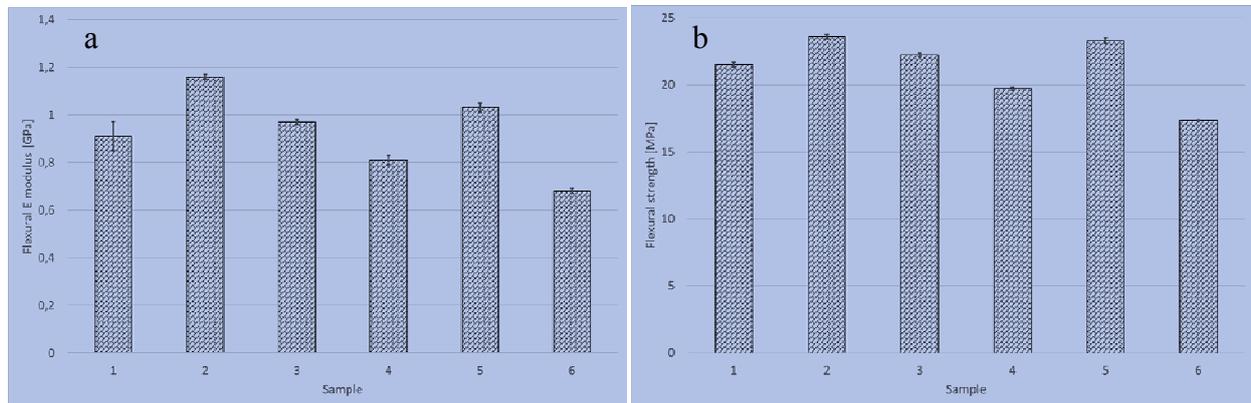


Figure 2. a) Flexural E modulus and b) flexural strength of the samples 1-6 (for designation see Table 1).

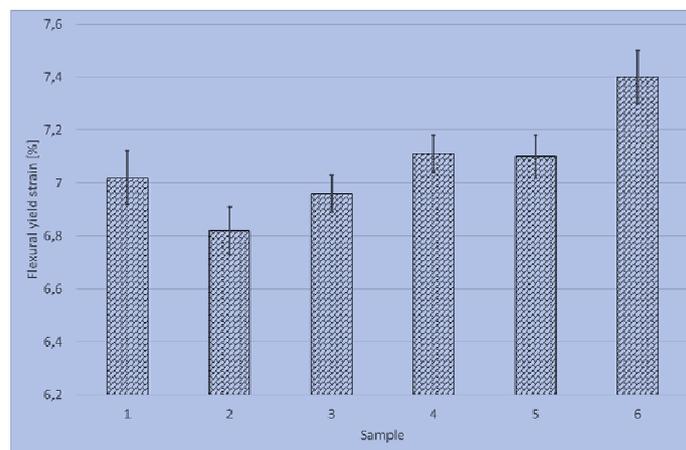


Figure 3. Flexural yield strain of the samples 1-6 (for designation see Table 1).

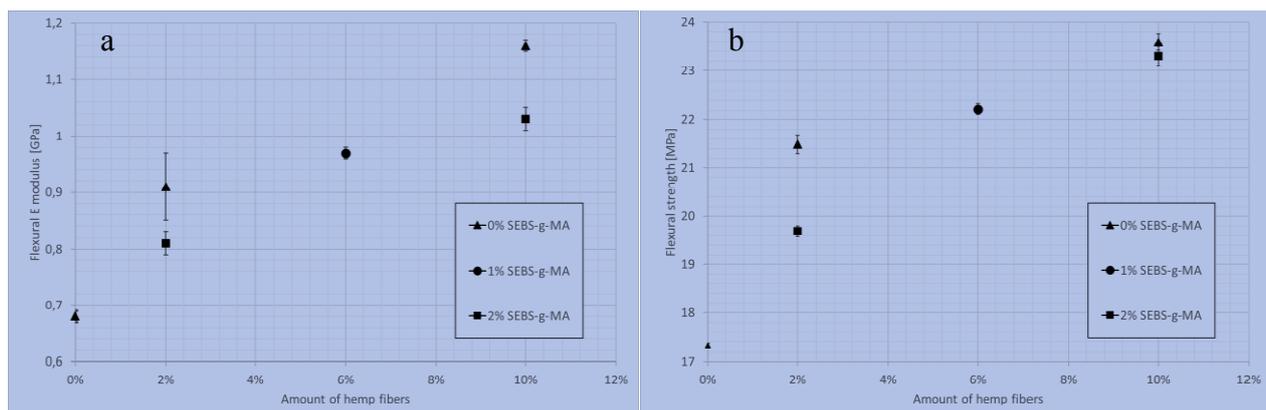


Figure 4. a) Flexural E modulus and b) flexural strength vs. hemp fibers content of the samples 1-6 (for designation see Table 1).

3.5. Tensile properties

The stiffness and tensile strength of the biocomposites increase with the addition of hemp fibers to green PE-HD, but, at the same time, the yield strain and strain at break are reduced. [14, 20, 21] The addition of SEBS-g-MA to green PE-HD/hemp

fiber biocomposites rises their stiffness and strength, but reduces the yield strain and strain at break. [14] (Figures 5-7) The biocomposite with 10 wt.% hemp fibers and 2 wt.% SEBS-g-MA has the highest E modulus and tensile strength, while the highest yield strain and strain at break are characteristic of neat green PE-HD. Higher E modulus and tensile

strength can be attributed to interfacial adhesion between all components in ternary blend. [15] The addition of SEBS-g-MA improves interactions between hemp fibers and green PE-HD matrix, so we can conclude that SEBS-g-MA is a good compatibilizer in this case. Improved interactions are confirmed also by ATR FT-IR measurements. For the calculation of E modulus of ternary blends, the Halpin-Tsai semi-empirical relation by rule of mixture

was chosen. For the E modulus of green PE-HD, hemp fibers and SEBS-g-MA, the values of 1.08 GPa, 5.0 GPa and 0.3 GPa, respectively, were taken. Calculated values for biocomposites with hemp fibers and SEBS-g-MA are lower than measured values due to faster crystallization rates, nevertheless, the calculated results correspond well with measured values. (Figure 7a)

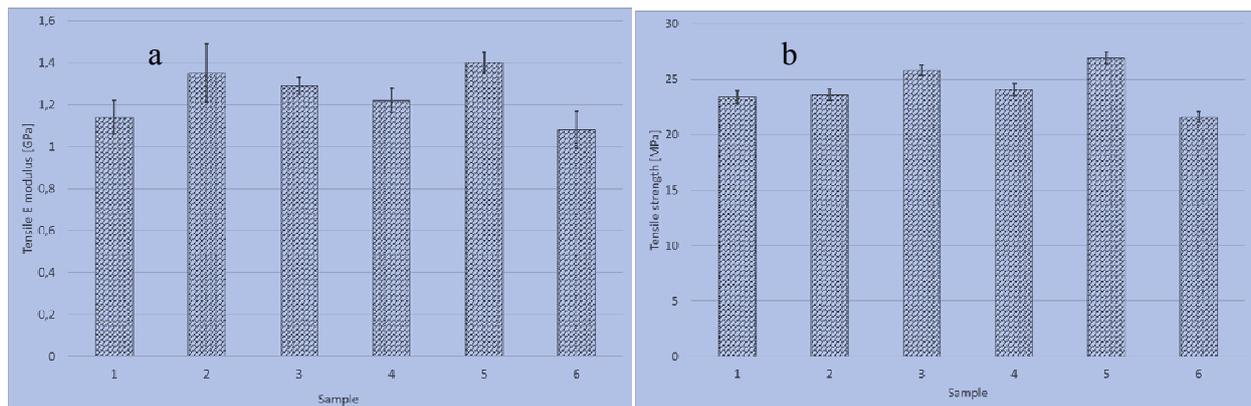


Figure 5. a) Tensile E modulus and b) tensile strength of the samples 1-6 (for designation see Table 1).

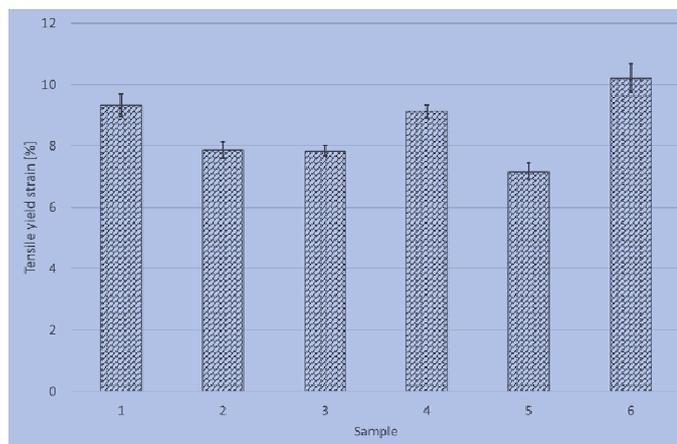


Figure 6. Tensile yield strain of the samples 1-6 (for designation see Table 1).

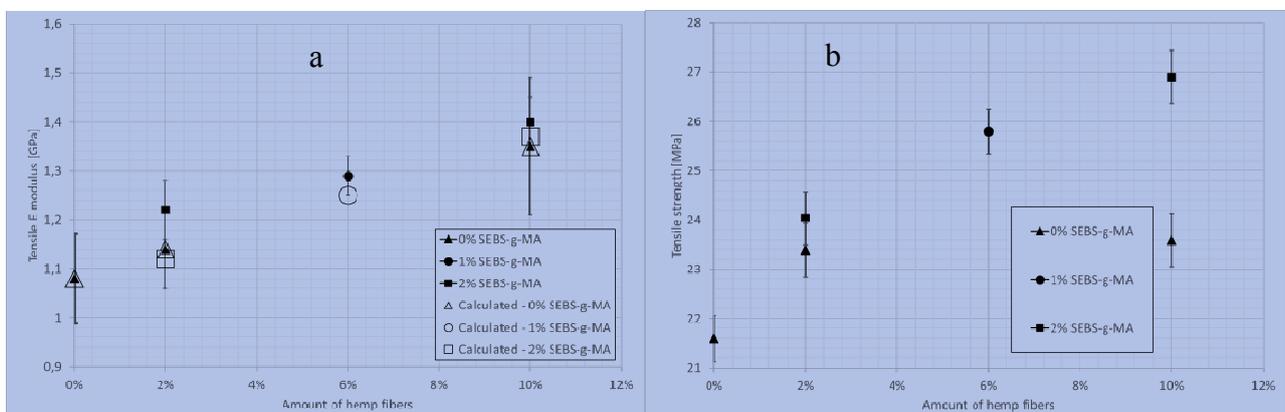


Figure 7. a) Tensile E modulus and b) tensile strength vs. hemp fibers content of the samples 1-6 (for designation see Table 1).

3.6. Flash DSC

The addition of hemp fibers rises the crystallization temperature also at cooling rate 10 K/s as at 1,000 K/s. In the same time, the addition of hemp fibers rises the melting temperatures of biocomposites. [14] (Table 4) The addition of SEBS-g-MA also rises the crystallization temperature as well at low as at high cooling rates. The melting temperature is at the addition of 2 wt.% hemp fibers and SEBS-g-MA higher, at 10 wt.% hemp fibers and

SEBS-g-MA is melting temperature lower. The crystallization rate, i.e. the reciprocal of the crystallization half time ($t_{0,5}$) shows nice dependence of the higher crystallization rate as well with the addition of hemp fibers as with addition of SEBS-g-MA. [14] We can conclude that the hemp fibers act as nuclei for the crystallization of green PE-HD and induce heterogenic crystallization. The addition of SEBS-g-MA also acts as nuclei for the heterogenic crystallization of green PE-HD [14] (Figures 8, 9).

Table 4. Crystallization and melting temperatures

Sample	$T_c(1\text{ }^\circ\text{C/s})$ [°C]	$T_c(1,000\text{ }^\circ\text{C/s})$ [°C]	T_m [°C]
1	116.0	91.0	121.4
2	116.1	93.2	130.1
3	117.2	93.1	130.0
4	116.3	93.2	127.5
5	116.2	95.3	128.4
6	110.5	77.6	119.8

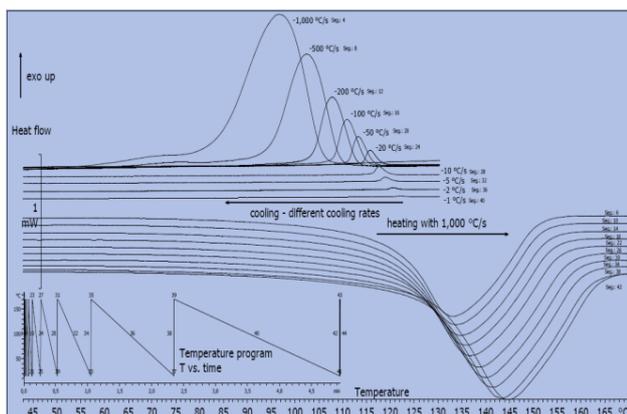


Figure 8. Flash DSC melting and cooling curves.

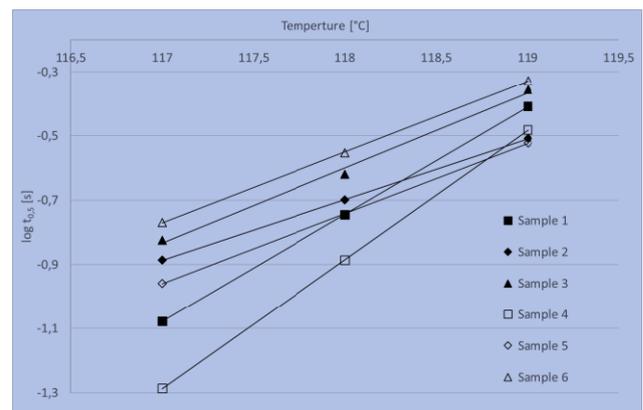


Figure 9. Temperature dependence of the crystallization half-time.

3.7. Impact properties

Notched impact strength (Figure 10) is not influenced by the amount of the added hemp fibers. The addition of SEBS-g-MA rises the notched impact strength. The highest notched impact strength had the sample with 2 wt.% hemp fibers and 2 wt.% SEBS-g-MA. At unnotched impact strength, the addition of 10 wt.% hemp fibers in green PE-HD

causes break of the samples, in all other mixtures the samples do not break. The addition of SEBS-g-MA rises both the notched and unnotched impact strength of biocomposites, especially at higher hemp fibers content. The results indicate on the enhanced interactions between green PE-HD matrix and hemp fibers with the addition of SEBS-g-MA due to higher interfacial adhesion, which acts as good compatibilizer [15].

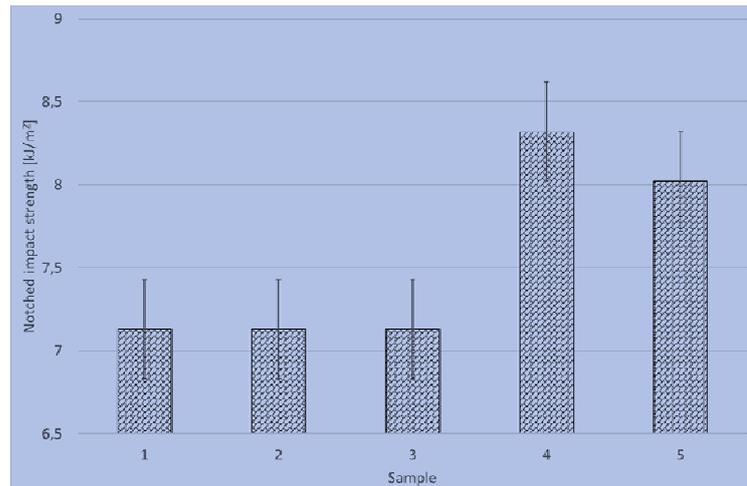


Figure 10. Notched impact strength of samples.

3.7. Scanning electron microscopy

SEM pictures (Figure 11) of biocomposites green PE-HD and hemp fiber without SEBS-g-MA show neat surface of hemp fibers without any trace of green PE-HD matrix. We can conclude that there are no interactions between matrix and fibers.

With the addition of SEBS-g-MA, the wettability of the hemp fibers with the green PE-HD

matrix was enhanced equally in the case of 2 wt.% hemp fibers as in the case of 10 wt.% hemp fibers. SEM pictures confirm previous test results and show that SEBS-g-MA is very good compatibilizer for the biocomposites green PE-HD and hemp fibers.

The morphology of the composites with SEBS-g-MA revealed efficient fiber-matrix interfacial adhesion. [15]

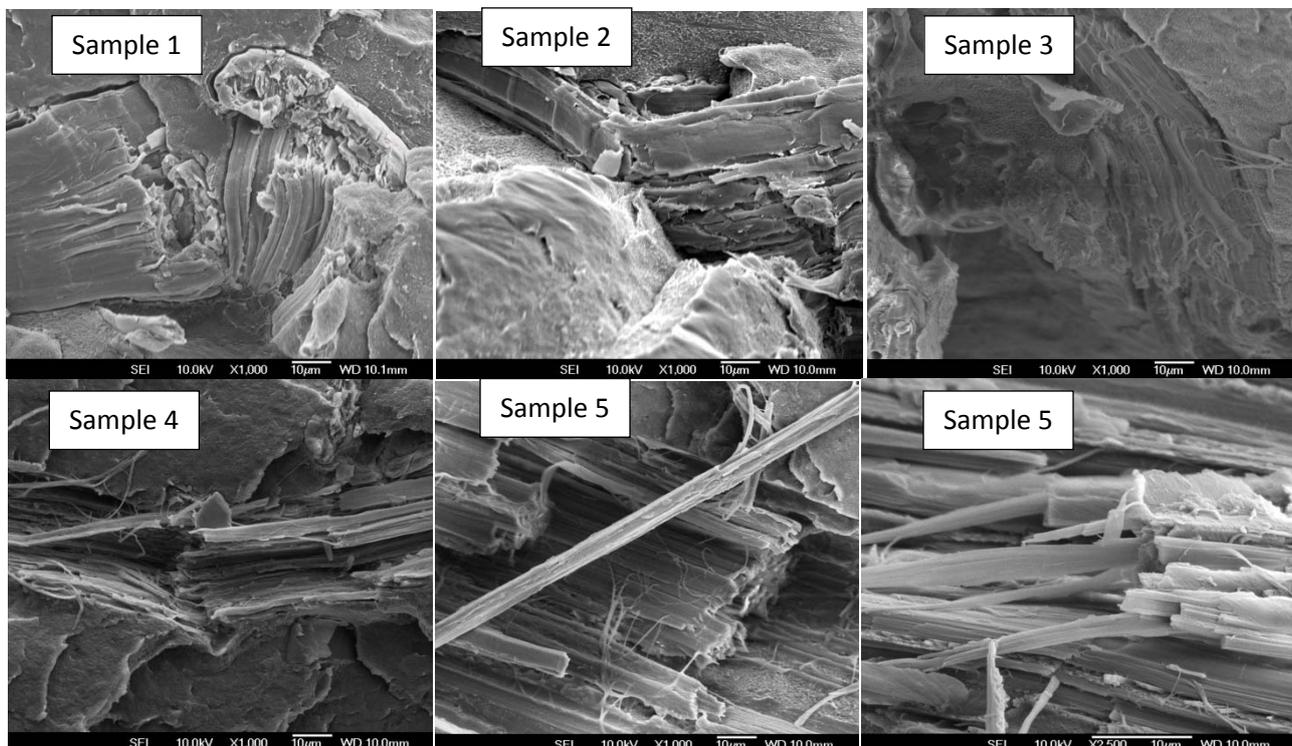


Figure 11. SEM pictures of samples 1 to 5 (for designation see Table 1).

4. CONCLUSIONS

We prepared the green PE-HD/hemp fiber/SEBS-g-MA biocomposites and investigated

the effectiveness of compatibilizer SEBS-g-MA. The mechanical and thermal properties were determined by using tensile and bending tests, DMA, Flash DSC and SEM. Tensile E modulus and tensile

strength of biocomposites with hemp fibers and SEBS-g-MA were higher as compared to neat green PE-HD. High E modulus and tensile strength indicate very good compatibility of the constituents of biocomposites, due to the compatibilizer SEBS-g-MA. The results of DMA and bending tests support the results of tensile test. E moduli of the samples without SEBS-g-MA are slightly higher than those of the samples with SEBS-g-MA. The thermal stability of biocomposites is for all samples drastically higher as compared to neat green PE-HD. As shown by DMA, E modulus at 100 °C increases from 80 % to 178 %. The melting point (T_m) and crystallization temperature (T_c) of biocomposites were determined by Flash DSC. T_m at the cooling rate of 10 °C/min is shifted from 120 °C (neat green PE-HD) to 121 °C and up to 130 °C, whereas T_c is shifted from 111 °C (neat green PE-HD) to 116 - 117 °C. At the cooling rate of 1,000 °C/min, T_c is shifted from 78 °C (neat green PE-HD) to 91 - 95 °C. Incorporation of SEBS-g-MA together with hemp fibers into the matrix enhanced strength, stiffness, impact strength and rises thermal stability due to good interfacial adhesion between hemp fibers and green PE-HD matrix. The novel biocomposites with the addition of the compatibilizer SEBS-g-MA are suitable for applications such as technical parts that require higher stiffness and thermal stability as compared to neat green PE-HD.

5. ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support of the EU project Poly4EmI, Voucher 2015 – Supporting initial cross-sectoral projects on the field of bio-polymers.

5. REFERENCES

- [1] N. Malhotra, K. Sheikh, S. Rani, *A Review on Mechanical Characterization of Natural Fiber Reinforced Polymer Composites*, Journal of Engineering Research and Studies, Vol. 3 (2012) 75–80.
- [2] K. P. Ashik, S. R. Sharma, *A review of mechanical properties of natural fiber reinforced hybrid polymer composites*, Journal of minerals and materials characterization and engineering, Vol. 4 (2015) 420–426.
- [3] D. Chandramohan, K. Marimuthu, *A Review of Natural Fibers*, Arpapress, Vol. 8–2 (2011) 194–206.
- [4] H. Ku, H. Wang, N. Pattarachaiyakoop, M. Trada, *A review on the tensile properties of natural fibre reinforced polymer composites*, Composites Part B Engineering, Vol. 42–4 (2011) 856–873.
- [5] A. G. Facca, M. T. Kortschot, N. Yan, *Predicting the elastic modulus of natural fibre reinforced thermoplastics*, Composites Part A: Applied Science and Manufacturing, Vol. 37–10 (2006) 1660–1671.
- [6] A. N. Inul, A. Ashak, *Effect of Fiber Loading and Compatibilizer on Rheological, Mechanical and Morphological Behaviors*, Open Journal of Polymer Chemistry, Vol. 2 (2012) 31–41.
- [7] S. Mohanty, S. K. Nayak, *Mechanical and Rheological Characterization of Treated Jute-HDPE Composites with a Different Morphology*, Journal of Reinforced Plastics and Composites, Vol. 25–13 (2006) 1419–1439.
- [8] N. Othman, H. Ismail, M. Mariatti, *Effect of Compatibilizers on Mechanical and Thermal Properties of Bentonite Filled Polypropylene Composites*, Polymer Degradation and Stability, Vol. 91–2 (2006) 1761–1774.
- [9] S. Mohanty, S. Verma, S. K. Nayak, *Dynamic Mechanical and Thermal Properties of MAPE Treated Jute/HDPE Composites*, Composites Science and Technology, Vol. 66–3/4 (2006) 538–547.
- [10] A. F. Vargas, V. H. Orosco, F. Rault, S. Giraud, E. Devaux, B. L. López, *Influence of Fiber-Like Nano-fillers on the Rheological, Mechanical, Thermal and Fire Properties of Polypropylene: An Application to Multi-Filament Yarn*, Composites: Part A, Vol. 41–12 (2010) 1797–1806.
- [11] M. Modesti, A. Lorenzetti, D. Bon, S. Besco, *Thermal Behavior of Compatibilised Polypropylene Nano-composite: Effect of Processing Condition*, Polymer Degradation and Stability, Vol. 91–4 (2006) 672–680.
- [12] P. W. Balasuriya, L. Ye, Y. W. Mai, *Mechanical Properties of Wood Flake Polyethylene Composites. Part I: Effects of Processing Methods and Matrix Melt Flow Behavior*, Composites Part A: Applied Science and Manufacturing, Vol. 32–5 (2001) 619–629.
- [13] R. M. Roweel, A. M. Tillman, R. Simonson, *A Simplified, Procedure for the Acetylation of Hardwood and Softwood Flakes for Flakeboard Production*, J. Wood Chem. Tech, Vol. 6 (1986) 427.
- [14] M. Pracella, M. Minhaz-UI Haque, V. Alvarez, *Functionalization, Compatibilization and Properties of Polyolefin Composites with Natural Fibers*, Polymers, Vol. 2–4 (2010) 554–574.
- [15] O. M. Jazani, A. Arefazer, M. H. Beheshy, *Study on the effect of processing conditions on the mechanical properties of PP/PC/SEBS*

ternary blends using Taguchi experimental analysis, e-Polymers, 117 (2010) 1–14.

[16] R. Huang, X. Xu, S. Lee, Y. Zhang, B.J. Kim, Q. Wu, *High Density Polyethylene Composites Reinforced with Hybrid Inorganic Fillers: Morphology, Mechanical and Thermal Expansion Performance*, Materials, 6 (2013) 4122–4138.

[17] J. E. K. Schawe, *Influence of processing conditions on polymer crystallization measured by fast scanning DSC*, Therm Anal Calorim, 116, (2010) 1165–1173.

[18] G. V. Poel, D. Istrate, A. Magon, V. Mathot, *Performance and calibration of the Flash DSC 1, a new, MEMS-based fast scanning calorime-*

ter, Therm Anal Calorim, Vol. 110 (2012) 1533–1546.

[19] H. Jena, M. K. Pandit, A. K. Pradhan, *Study the Impact Property of Laminated Bamboo-Fibre Composite Filled with Cenosphere*, International Journal of Environmental Science and Development, Vol. 3–5 (2012) 456–459.

[20] E. Lezak, Z. Kulinski, R. Masirek, E. Piorkowska, M. Pracella, K. Gadzinowska, *Mechanical and thermal properties of green polylactide composites with natural fillers*, Macromol. Biosci., Vol. 8 (2008) 1190–1200.

[21] R. Karnani, M. Krishnan, R. Narayan, *Biofiber-reinforced polypropylene composites*. Polym. Eng. Sci, Vol. 37 (1997) 476–483.



ТЕРМАЛНА И МЕХАНИЧКА СВОЈСТВА БИОКОМПОЗИТА БАЗИРАНИХ НА ЗЕЛЕНОМ РЕ-HD И ВЛАКНИМА КОНОПЉЕ

Сажетак: Биокompозити од влакана конопље ојачани био-базираним полиетиленом велике густине (зелени РЕ-HD) су припремљени коришћењем малеинског анхидридног графтираног стирен-етилен/бутилен-стирена (SEBS-g-MA) као компатибилизатора. Неколико композиција биокompозита је припремљено на двопужном екструдеру коришћењем потпуног факторског дизајна на ком су се мијењала два фактора са два нивоа. Механичка и термална својства узорака тестирања, припремљена ињекцијским моделовањем, испитивана су тестирањем влачне чврстоће и савијања, DMA, и ултрабрзом диференцијалном динамичком калориметријом (Flash DSC). Велика тврдоћа и јачина биокompозита у поређењу са једноставним зеленим РЕ-HD индицира веома добру компатибилност саставних дијелова. Тврдоћа узорака без SEBS-g-MA је нешто мало већа од узорака са SEBS-g-MA. Термална стабилност биокompозита је за све узорке драстично већа у поређењу са једноставно зеленим РЕ-HD. Температуре топљења (T_m) и кристализације (T_c) биокompозита се пребацују на више температуре. Инкорпорација SEBS-g-MA заједно са влакнима конопље у матрици јача снагу, тврдоћу, чврстоћу и подиже термалну стабилност. Нови биокompозити су погодни за примјену као технички дијелови, што захтијева већу крутост и термалну стабилност у поређењу са једноставно зеленим РЕ-HD.

Кључне ријечи: полиетилен велике густине (РЕ-HD), влакна конопље, малеински анхидридни графтирани стирен-етилен/бутилен-стирен (SEBS-g-MA), карактеризација.

