Effect of compatibilizing agents on the interface and mechanical behaviour of polypropylene/hemp bast fiber biocomposites

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Abstract. During the last years automotive industry has given a lot of attention to the biobased polymers that are sustainable and eco-friendly. Nevertheless fully green composites are currently too expensive for most applications. A viable solution and logical starting point at this material revolution lies in reinforced synthetic thermoplastics based on plant derived biodegradable fibers. Plant fibers (PF’s) have potential to reduce weight of composite vehicle parts up to 40% compared with the main automotive composites filler, glass fibers (GF’s). Production of GF’s composites is much more energy intensive and polluting compared with growing, harvesting and preparing of PF’s. The main disadvantage of PF’s lies in combination of non-polar hydrophobic polymer matrix and polar hydrophilic fibers. This combination creates poor interface with low adhesion of both components. That implies poor wettability of fibres by polymer matrix and low mechanical properties of biocomposites. Therefore specific compatibilizing agents (Struktol SA1012, Fusabond P353, Smart + Luperox) were used in order to enhance compatibility between reinforcement and matrix. In this paper sets of biocomposite compounds were prepared by twin screw extrusion considering different type and weight percentage (wt. %) of compatibilizing agents, hemp bast fibres (HBF’s) within ratio 20 (wt. %) and polypropylene (PP) THERMOFIL PP E020M matrix. Resulting compounds were than injection molded and tested samples were characterized by means of scanning electron microscopy (SEM) and mechanical testing.

1. Introduction
Producing the conventional composites is energy intensive and polluting, while their durability is often seen as an advantage, on the other hand it is also their biggest disadvantage. Glass, carbon, and aramid fibre reinforced polymers do not degrade naturally, it is hard to dispose of and difficult to recycle them [1]. Glass fibres compared to aramid and carbon fibres are the most widely used reinforcement due to their low cost and relatively good mechanical properties. However, these fibres have serious drawbacks as indicate table 1 [2]. But to meet European Union directive about end-of-life of vehicles (ELV), which requires that 95% of all new vehicles should be recyclable by 2015, there is strong need to find new and more suitable solutions. Thermoplastics offer some solution, as the resin could be
thermally recycled [1]. Variety of automotive components based on environmentally friendly reinforced fibre polymers are now manufactured instead of glass [2]. There are already companies (Lear Corp., Johnson Controls Inc., Ford, etc.) using hemp fibers as reinforcement in number of automotive components like door trim panels and trunk trims [3].

### Table 1. Comparison between natural and glass fibres [2].

|                        | Natural fibres | Glass fibres            |
|------------------------|----------------|-------------------------|
| **Density**            | Low            | Twice that of natural fibres |
| **Cost**               | Low            | Low, but higher than NF  |
| **Renewability**       | Yes            | No                      |
| **Recyclability**      | Yes            | No                      |
| **Energy consumption** | Low            | High                    |
| **Distribution**       | Wide           | Wide                    |
| **CO₂ neutral**        | Yes            | No                      |
| **Abrasion to machines** | No                       | Yes                     |
| **Health risk when inhaled** | No                               | Yes                     |
| **Disposal**           | Biodegradable  | Not biodegradable       |

The modern fibre corps production oriented on high yield requires huge amounts of water, pesticides, fungicides, and herbicides. Those factors, with the other agricultural techniques, like monorops growth without crop rotation and tillage are contributing to soil degradation. In consequence this could lead to disruption of ecological balance. Nevertheless, fibre crops as a renewable resource of PF’s could be important for world environment, economy and sustainable future [4].

Compared to the other fibre crops, production of Hemp (Cannabis sativa L.) is easy to achieve organically. Therefore many of the ecological problems in chemical farming could be avoided [5]. Hemp, considered as one of the oldest crops known to man and has been cultivated at least 12,000 years [4]. During 19<sup>th</sup> century heavy taxes was imposed on industrial hemp that essentially legislated the industry out of existence [6]. Recently interest has been renewed, possibility of agro-ecological cultivation and hemp products sustainability are the main drivers for a future expansion of this multifunctional crop. The economical value of hemp growing can be related to the possibility of very large number of end-use applications (figure 1). Traditionally, hemp had a very important position in crop rotations because it restores nutrients to the soil, thus provide beneficial effect on following crops [5]. Gorchs et al. [7] reported increased yield of wheat grown after hemp rotation. Moreover, very high yield compared with many other crops, up to 25 tons (t) above ground dry matter per hectare (20 t·ha<sup>-1</sup> stem dry matter), depending on environmental conditions and agronomy [8]. Other benefit of hemp is that it can be grown on polluted areas and can contribute to phytodepuration (reduction of contaminants in waste water by means of biological and physicochemical processes driven by aquatic photosynthetic organism) [9]. Despite of many positive features of hemp, there still barriers which are needed to be overcome: improvement of mechanical and biological processing for fiber separation; innovation of harvesting and agro-production systems; legislation related to progressive lowering of the legal delta-9-tetrahydrocannabinol (THC) limit content in plants, seeds availability limitation and so on [5].

The main disadvantage of those biocomposites is combination of non-polar hydrophobic polymer matrix and polar hydrophilic fibers. This combination creates poor interface with low adhesion of both components. That implies poor wettability of fibres by polymer matrix and low mechanical properties of biocomposite. Due to this it is necessary to modify HBF’s surface properties prior to using them as reinforcement to ensure good dispersion and mechanical properties. In this paper, chemical
modification of the fiber-matrix interphase with different compatibilizing agents for comparison was used. Generally, coupling agents have two functions to ensure proper stress transfer at the interface between fiber and matrix. The first function is to react with surface OH groups of cellulose and the second is to react with functional groups of the matrix [1].

Figure 1. Main uses of the hemp products.

2. Experimental

2.1. Materials

Hemp bast fibres were purchased from Atelier Johanna (CZ). Coupling agents were purchased as follows: Fusabond P353 - DuPont (USA), Struktol SA1012 - Struktol Company of America (USA), Smart + Luperox - DoW Corning Corporation (USA). Matrix polypropylene THERMOFLIP PP E020M was purchased from Sumika Polymer Compounds (EU).

2.2. Preparation of hemp bast fibers (HBF)

For the composite material preparation, fibres were milled at the shear mill (RETSCH SM 300) (n = 3000 min⁻¹) with trapezoidal holes of 0.75 mm to modify their length. Subsequently, fibres were washed with deionized water to remove organic impurities and greases. Milled fibres were then dried. An optical microscope (Leica DM 2005P) was used to analyze the length of fibres (at least 30 individual fibres were observed). Range of fibres lengths were within 0.5 mm up to 2 mm.

2.3. Compounding procedure

For fabrication composite pellets was used twin screw extruder (ZAMAK EHP-2x130di) flowed by water bath and pelletizer. Temperature profile of extrusion line was set to 150°C up to 180°C. Coupling agents and matrix were dosed directly to hopper. HBF was dosed directly into the melting chamber of extruder in the recommended front position by external device, working on the gravimetric principle. The reason for dosing fibres in the front parts of the extruder (near granulation head) is to prevent excessive shear stress of fibres during compounding melt composite and thus their damage or thermal degradation.
2.4. Drying
Due to the fact that in the previous operation extruded string passed through a water bath, it was necessary to dry granulated composite compound. For drying (80°C, 6 hours) was used a stationary laboratory oven (Venticell). Moisture would adversely affect workability and properties (dimensional changes) of the final molded part, for this reason it was necessary to reduce the moisture content to the lowest possible level.

2.5. Injection molding
Further than were injection molded testing specimens according to ISO 527. Based on the experimental tests on injection molding machine (ARBURG 270S 400-100) was chosen increasing temperature profile (160°C up to 180°C) of the melting chamber.

2.6. Mechanical testing
The mechanical properties were measured according to international standards (table 2). Testing machines for measuring mechanical properties were used as follow: Tensile - TIRA test 2300, Impact - CEAST Resil 5.5 and Flexural - Hounsfield H10KT.

| Coupling agents: | 1,5% SMART + 0, 2% LUPEROX P353 | 4% FUSABOND P353 | 3% STRUKTOL SA 1012 |
|------------------|----------------------------------|-----------------|---------------------|
| MATRIX / FIBRE   | PP + 20% HBF                     | PP + 20% HBF    | PP + 20% HBF        |
| Tensile Modulus of Elasticity (1 mm/min) | ISO 527/1B/1 | 1596 | 1419 | 2143 | 1395 | 1917 | 1337 | 1992 |
| Yield Strength (Ultimate Strength) (50 mm/min) | ISO 527/1B/50 | 26,7 | 29,7 | 37,3 | 27,7 | 34,9 | 27,6 | 33,7 |
| Nominal Strain at Fracture (50 mm/min) | ISO 527/1B/50 | 39,4 | 38,0 | 8,9 | 30,5 | 7,1 | 20,3 | 5,8 |
| Charpy Impact Energy (+23°C) | ISO 179-1/1eA | 8,8 | 10,1 | 5,6 | 7,7 | 4,7 | 8,3 | 4,5 |
| Charpy Impact Energy (+35°C) | ISO 179-1/1eA | 3,8 | 3,4 | 3,6 | 3,3 | 3,0 | 3,1 | 2,9 |
| Flexural Modulus of Elasticity (2 mm/min) | ISO 178 | 1287 | 1427 | 2064 | 1305 | 1929 | 1193 | 1859 |
| Flexural Strength (2 mm/min) | ISO 178 | 34,8 | 39,2 | 49,5 | 35,9 | 47,3 | 34,7 | 44,3 |

2.7. Scanning electron microscope (SEM) examination
Micrographs of PP/HBF composite fractures were taken on scanning electron microscope Tescan Vega XMU. To investigate adhesion of fibres and interface improvement according to used coupling agents were taken fractures from Charpy impact energy measurements under low temperatures (-35°C).

3. Results and discussion

The effect on interface and mechanical properties of resulted PP/HBF biocomposites were investigated due to use of compatibilizing agents based on different bonding principles. The concentrations of compatibilizing agents were used due to producer’s recommendations and experimental tests.

Fusabond P353 (F) is one of the most commonly used compounding agents. This additive is on the basis of maleic anhydride (MA) which is by the producer grafted (g) with PP chains. Grafting is usually carried out by radical mechanism, as an initiator there is peroxide group which by the reaction with the PP chain creates free radical which subsequently reacts with the PP molecule at creation compound MA-g-PP. PP connected on the MA is during compounding physically implemented into PP matrix by which there is complete interlacing of the PP matrix with natural fibres.

Struktol SA 1012 (S) is compatibilizer and processing additive designed to deliver better physical properties and dispersion. Struktol has a similar function as additive already mentioned above. There is difference between free radical creations, which enable connection of the polar and non-polar composite components. Covalent bond is created by the ion mechanism initiated by the additive hydrolysis.

Smart + Luperox (SL) is two component liquid additive based on patent invention No. WO 2011/083045 A1. The above mentioned coupling technologies functionalize polypropylene using grafting that is accompanied by degradation of the polymer by $\beta$-chain scission. Such degradation results in a decrease of the viscosity of the material to be processed. Furthermore, this degradation results in a polymer having inferior performance compared to the starting material. Compared to this, PP, the unsaturated silane and the compound capable of generating free radical sites (peroxide) in the PP are mixed together before twin screw extrusion process at ambient temperature. The hydrolysable groups, for example silyl-alkoxy groups, present in the silane moieties grafted to the PP react in the presence of ambient moisture with hydroxyl groups on HBF surface.

3.1. Mechanical properties

The mechanical properties are generally affected by the volume fraction of the added reinforcement (HBF), the dispersion of the HBF in the matrix and the improvement of interaction between the HBF and the matrix by compatibilizing agents. Summarization of mechanical properties is in table 2.

A maximum tensile modulus of 2143 MPa (34% increase compared to pure PP control sample) was achieved for PP/HBF treated with SL compatibilizing agent. The results for tensile strength showed with same compatibilizing agent (SL) best improvement of 37.3 MPa (40% increase compared to control sample). The strain at break was reduced significantly for all PP/HBF reinforced composites. The largest decrease of 85% was achieved for S compatibilizing agent and lowest decrease of 77% for SL compatibilizing agent. The reason is that stiff HBF caused substantial local stress concentrations and failure at strain. The impact strength of PP/HBF reinforced composites also significantly decreased for booth temperatures and all compatibilizing agents. The highest impact strength at 23°C of 5.6 kJ/m$^2$ (36% decreasing) was achieved again for SL compatibilizing agent and lowest 4.5 kJ/m$^2$ (49% decrease) for S compatibilizing agent. The only little energy is absorbed to break samples at low temperatures (-35°C) for all PP/HBF composites. This decrease for booth temperatures may be attributed to the fact that the notch serves as the stress concentration zone and under sudden impact, fracture is very easily propagated. The booth flexural modulus and flexural strength increased for all PP/HBF treated with compatibilizing agents. The highest values attained for flexural modulus (2064 MPa, 60% increase) and strength (49.5 MPa, 42% increase) showed SL compatibilizing agent. The lowest values attained for flexural modulus (1859 MPa, 44% increase) and strength (44.3 MPa, 27% increase) showed S compatibilizing agent.
3.2. Interfacial properties  
The SEM micrographs of Charpy impact fractures of PP/HBF composites treated with compatibilizing agents under low temperatures (-35°C) are shown at figure 2. To improvement of mechanical properties with addition of compatibilizing agents were confirmed above. As can be seen all three micrographs showed embedded HBF in PP matrix with very tight interface. That implies significant improve of HBF wettability and interface adhesion of both components.

![Figure 2. SEM micrographs of PP/HBF composite fractures treated with compatibilizing agents: A) Smart + Luperox, B) Fusabond P353, C) Struktol SA1012.](image)

4. Conclusion  
In this paper, PP/HBF composites modified with compatibilizing agents based on different bonding principles have been investigated due to processing and industrial applications such as injection molding. Hemp bast fibres have properties that make them a suitable eco-friendly replacement compared to glass fibres. The economical value of hemp growing can be related to the possibility of very large number of end-use applications and possibility of organic growing can be related to environmental and sustainable production. These composites have shown promising mechanical
properties. However, impact strength represents the lowest mechanical property affected by compatibilizing agents. It was found that Smart + Luperox compatibilizing agent based on silane has shown best improvement in mechanical properties. The lowest mechanical properties were found for Smart SA 1012 compatibilizing agent. In conclusion it can be postulated that, all used compatibilizing agents can serve as a value added and cost effective improvement in biocomposite material processing based on HBF.

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