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BIODEGRADABLE COMPOSITES WITH HEMP

Edgars Kirilovs, Silvija Kukle
Riga Technical University, Institute of Textile Materials Technologies and Design
Azenes street 14/24, LV 1048 Riga, Latvia
ph: +(371) 67089816, fax: +(371) 67089160, e-mail: edgars.kirilovs@rtu.lv

Abstract

The scientific researches to get more environmentally friendly and also cheaper, and more sustainable materials that can be differently exploited have been encouraged by the increase in environmental awareness. Industrial hemp stands between the strongest natural fibers available- their main advantage is low cost material and low energy requiring material in production.

It has been showed that hemp can be used as a part of composite material to create more renewable, more environmentally friendly and innovative material. The composite material can have different fiber structure- long or short fibers can be oriented long or short parallel, long or short random, or cross-ply. Eco- composites can be combined by natural fiber and biodegradable polymer matrix. Also the biodegradable matrices can be bought as commercial products and, what is more, the price of these materials is higher and that is one of the largest restrictions for their wider using.

Analysis starts with the extracting process of the fiber, then comes the using phase and recycling. In the paper there is showed possible usage of hemp components in the structure of conventional composites and biodegradable composites that will be used for office interior and equipment. There are also showed results of the researches to create new board material that are planned to be used in furniture and equipment production for usage in public sector so replacing the traditional materials.

Key words: *biodegradable composite, mechanical properties, natural fiber, water absorption, renewable resources, polypropylene*

1.INTRODUCTION

Plastic composites that are strengthened with the natural fibers are demanded raw materials in many economical sectors including vehicle industry, building and furniture manufacturing. In the former practice while making the plastic composites, the armature wood or textile fibers (predominantly synthetic) are implemented in the plastic matrixes. Natural fibers are environmentally friendly, completely recyclable, widely available, and regularly renewable, comparatively cheep, with sufficiently good physical and mechanical qualities, with low density – plant fibers are lighter than glass, carbon or aramid fibers (Table 1). If the natural ability of decomposition solves ecological problems, then low costs and good qualities makes economical interest. Natural fibers recycling at the end of the life cycle by burning or in the waste polygon, exempted volume of CO_2 balances the volume that is received during the growth. Abrasive qualities of natural fibers are much lower which ensures benefits in the treatment of composite material. Natural fiber composites are completely recyclable at the end of their lifetime which makes them nature friendly materials. These are also renewable resources contrary coal, oil and natural gas. In the composite materials which are made by using unmodified plant fibers required mechanical qualities are not reached very often. To avoid it before the making the composite in many cases additional treatment of the surface or usage of reagents is necessary.

So that materials could be classified as biodegradable, they must meet specific criteria set by the European standard EN 13432 [1] and define biodegradable plastics as one which is experiencing major changes in the chemical structure under specific environmental conditions. Biodegradable plastics submit degradation as a result of influence of the natural micro organisms - bacteria and fungi. In most of the international standards it is required that at least 60% of corrosive product need to be corrosed in 180 days. Plastics can be created as photo corrosive, corrosive as the result of oxidation, hydrophytes - corrosive, or one who may be decomposed.

Scope of testing under EN 13432 [1]:

* Chemical test: Disclosure of all constituents, threshold values for heavy metals are to be adhered to.
* Biodegradability in watery medium (oxygen consumption and production of CO_2): Proof must be made that at least 90% of the organic material is converted into CO_2 within 6 months.
* Disintegration in compost: After 3 months' composting and subsequent sifting through a 2 mm sieve, no more than 10% residue may remain, as compared to the original mass.
* Practical test of compost ability in a semi-industrial (or industrial) composting facility: No negative influence on the composting process is permitted.
* Compost application: Examination of the effect of resultant compost on plant growth(agronomic test), Eco toxicity test.

	Fibre							
	E-glass	flax	hemp	jute	ramie	coir	sisal	cotton
Density ($g.cm^3$)	2,55	1,4	1,48	1,46	1,5	1,25	1,33	1,51
Tensile strength (MPa)	2400	800-1500	550-900	400-800	500	220	600-700	400
Elongation (%)	3	1,2-1,6	1,6	1,8	2	15-25	2-3	3-10
Young's Modulus (Gpa)	73	60-80	70	10-30	44	6	38	12
Moisture absorption (%)	-	7	8	12	12-17	10	11	8-25

Table 1. The comparison of physical properties of natural and glass fibre

2. MATERIALS AND METHODS

2.1. Composite material

The natural fibers that are more researched lately are hemp fibers. Although hemp usage in natural fiber composites is relatively new market it has proved itself already in a good way. Hemp composites work well in different ways – if water absorption and exuding is necessary, thermal and acoustic isolation, firmness and hardness. Since hemp and other natural fibers usually are used in the polypropylene matrix (or with other polymers), the saving of manufacturing energy results in the glass fiber replacement and bigger proportion of natural fiber in the matrix. Consumption of energy for manufacturing glass fibers is five times bigger than needed for hemp fiber refinement, for manufacturing epoxy resin it is 10-20 times bigger.[2]

Advantages and disadvantages determine the choice: [3]

Advantages of natural fibres:

+ Low specific weight, which results in a higher specific strength and stiffness than glass.
This is a benefit especially in parts designed for bending stiffness.

+ It is a renewable resource, the production requires little energy, CO_2 is used while oxygen is given back to the environment.

+ Producible with low investment at low cost, which makes the material an interesting product for low-wage countries.

+ Friendly processing, no wear of tooling, no skin irritation

+ Thermal recycling is possible, where glass causes problems in combustion furnaces.

+ Good thermal and acoustic insulating properties

Disadvantages of natural fibres:

- Lower strength properties, particularly its impact strength
- Variable quality, depending on unpredictable influences such as weather.
- Moisture absorption, which causes swelling of the fibres
- Restricted maximum processing temperature.
- Lower durability, fibre treatments can improve this considerably.
- Poor fire resistance
- Price can fluctuate by harvest results or agricultural politics

2.2. Composite matrix

In many usages in a shape of matrix fiber, granule or polythene **PP** (Polypropylene) is used, which is thermoplastic, colorless (white) polymer with high melting temperature (158-170C^o) and high tension durability. It is widely used in engineering industry, textile industry, building, furniture manufacturing and in other industries. PP is resistant against different organic liquids, alkali, acids, poorly absorbs water. Polymer submits well to the recycling and in the composites with natural fibers it is partly biodegradable. PP is the most widely used thermoplastic material in the industry of natural fiber composites because of its low density, excellent processing, good mechanical qualities, high temperature resistance, good shape stability and resistance of the influencing strength. Increase of the PP usage describes also wide research and publications that are dedicated to the research of this material. Advantages and disadvantages of the polypropylene matrix are visible in the Table 2.

It is well known that unfilled polymers behave in either of two characteristic ways in tensile tests:

1) Brittle fracture of speciments at relatively small strains (</= 10%)
2) Ductile failure of specimens preceded by formation of a “bottleneck” at high deformations (tens or hundreds %) [5]

PP advantages	PP disadvantages
Low specific gravity (density)	Flammability
Excellent chemical resistance	Low- temperature brittleness
High melting point (relative to volume plastic)	Moderate stiffness
Good stiffness/ toughness balance	Difficult printing, painting ang gluing
Adaptability to many converting methods	Low UV resistance
Great range of special- purpose grades	Haziness
Excellent dielectric properties	Low melt strength
Low cost (especially, per unit volume)	

Table 2. Advantages and disadvantages of polypropylene matrix [4]

Matrix	Density (g/cm^3)	Melt Temp (°C)	Tensile Strength (Mpa)	Young Mod. (GPa)	Elong. To Break (%)
High density Polyethylene (HDPE)	0,94- 0,96	120- 130	32	1,1	150
Low density Polyethylene (HDPE)	0,91- 0,93	105- 115	20	0,2- 0,3	300- 600
Polypropylene (PP)	0,9	176	35	1,1- 1,6	150
Poly (lactic acid) (PLA)	1,25	140- 152	48	3,8	2,5
Poly (hydroxybutyrate) (PHB)	1,25	175	40	3,5	6
Polybutyleneadipate/ terephthalate (PBAT)	1,25- 1,27	110- 120	35	<0,2	560- 700

Table 3. Mechanical properties of polymers that are used a s matrixes in fibre composites [6]

2.3. Creation of composite materials

Fibers in the composite material work as intensifier while the pressure is directed from the matrix to the fibers as a result of interaction. Geometrical factors that separate different fiber composites are:

1) Fiber amount; 2) Fiber length; 3) Fiber allocation; 4) Fiber orientation.

Such layers can consist not only from the adjusted fibers but also from the differently oriented fibers. They can be located differently, for example, in the composite order or in the right angle one against another.

Theoretically the maximum amount in the composite can reach 91% which can be created if fibers are placed in the twisted shape. Fiber amount in the location prevalently reaches 45 -65%, but it is possible to reach also 70%.

Composite can have various fibers' structure as it is shown in Figure 1.

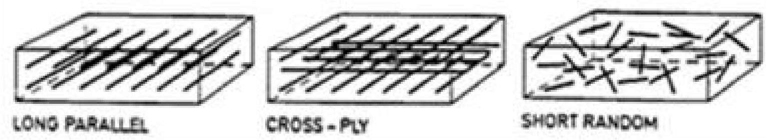
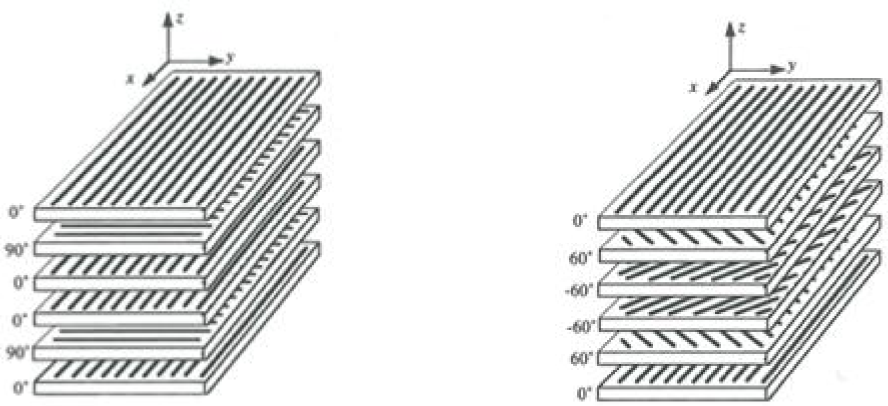


Figure 1. Fiber structure in composite

High performance polymer components usually consist of layers or in layers which are arranged in particular order. In order to anticipate total material flexibility, each layer is considered as homogeneous in a way that fiber planking and layout is equal in all the material. Fibers can be short or long, laid out in one or several layers in one or various directions. If the fibers are laid in one layer it is called *ply* but if it is laid in several layers it is called a *laminate*. Flat laminate is made from one direction laid fiber layers that are arranged in the angle of 90^{o} one above another. This is a typical construction that is used in the aircrafts because of its strength.

Simple condition is used to describe the layer sequences. It is described with simple layers. As you can see in the figure 3a layers are formed in 0^{o}/ 90^{o}/ 0^{o}/ 0^{o}/ 90^{o}/ 0^{o}, which can be simplified to [0/ 90/ 02/ 90/ 0], where digit 2 means that there are two layers with 0^{o} orientation. As in this case claddings are in the symmetric relation to the middle layer, then it is possible to simplify the designation [0/ 90/ 0], which means that layers repeat symmetrically. Similar is also the situation that is shown in the Figure 2 (b) where [0/ +60/ -60/ +60/ 0] is shortened to [0/ +60/ -60] or [0/ +-60]. [7]



(a) (b)

Figure 2. Arrangement of plies in (a) a crossply laminate and (b) an angle-ply laminate sandwiched between 0^{o} plies [7]

Composites reinforced with natural plant fibers have also negative aspects like unconformity between hydrophile natural fibers and hydrophobe thermoplastic and termoset matrix, wherewith it is necessary to use appropriate physical and chemical processing methods to improve adhesion between fiber and matrix.

2.4. Usage of biodegradable polymers

In year 2009 demand for biodegradable polymers in North America, Europe and Asia made the main part of the worlds' consumption. Despite the economic crisis that covered chemistry and plastic industries, in the market of biodegradable polymers there was an increased demand visible at 5-10% (comparing with year 2008). Total consumption of polymers in these three regions for 5 years period (year 2009-2014) is forecasted with the average growth of 13%. In year 2009 Europe has been the biggest biodegradable polymer consumer between the mentioned regions, using approximately half of the total amount in the world (Figure 3). [8]

In Figure 4 there is showed the use of fiber reinforced plastic in the percentage of different industries.

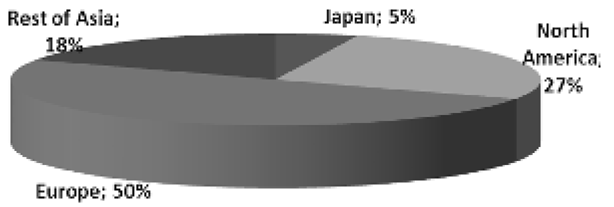


Figure 3. The use of biodegradable polimers in the World in 2009[8]

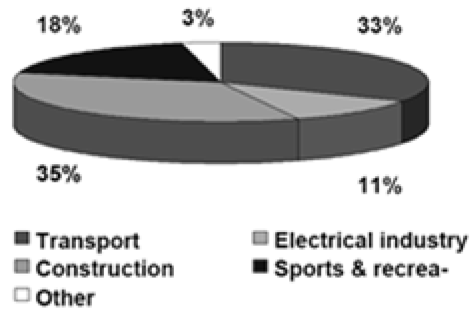


Figure 4. The use of polimer materials reinforced with fibers [9]

Main driving forces are established legislation that is not yet arranged in Latvia, pressure from the retailers, increasing consumer interest about sustainable plastic solutions, independence from the petrified oil and gas. The processes are encouraged also by reducing nature resources and restrictions of CO_2 emission. [8]

Creation of ecological life and work environment is not supposed without usage of wide constructions and design materials that next to good biodegradability have also good exploitation qualities.

Already today in the engineering industry in several cars building companies several components in the dash-boards, salons are replaced with biocomposites that allow reducing the weight, therefore also consumption of energy and ensuring consumers with friendlier salon environment, eliminating consumption of nonrenewable resources, liquidation of nature friendly vehicles.

2.5. Future of biodegradable plastic

A big challenge for the designers is the understanding of the today's needs because a long time the highest demand was after all that was described as "rare, exotic, special" and where different type of products and materials were hard to incorporate. It is clear that in the period before manufacturing, the creation of the material was considered as very important process and the design of the product already after that submitted the created material; in the period of manufacturing the final outlook of the product should be so standardized that creation of the material is only routine and not anymore the active research process.

In the biodegradable plastic industry it is still possible to develop and expand. The emissions level of carbon dioxide that develops from the recycling of the regular plastic is very high. After complete change of manufacturing the plastic that is made from the oil base to the plastic that is made using the renewable resources, it could be possible to balance level of carbon dioxide in the atmosphere. Still it is naive to hope of the possibility that in the near future traditional polymers completely would be replaced by nature friendly biodegradable polymers. The situation could be a little bit improved by creating and developing special market trend. Active research process is the one that is necessary in order to create new alternatives for materials – materials that don't stop the life process, don't pollute the air, water and earth.

To implement natural materials in usage is very hard process. It should start with the change of global consumer vision to the materials that he wants to buy. Consumer should choose to use the material that not only looks natural but that is natural. It can be changed only with the change of global thinking to separate industrially manufactured and natural materials and to understand what the influence of these materials on human and environment is. In order to reach the nature friendly goal, it is dependent from the design of the products, marketing, recycling, information, distribution, selling and waste control. Why should biodegradable material be considered to be better than its predecessor (energy ineffective and polluted)? How a material which includes several life cycles will be considered as Valuable? Mainly attention should be draw to three principles - (1) without garbage, (2) think about environment in every stage of the product, (3) redefine phrase "Valuable material" to "support for the life".[10]

Despite the mentioned, biopolymer industry has positive future, because nonrenewable resources are rapidly decreasing, its extraction becomes more expensive, and greenhouse effect is becoming more menacing in almost all parts of the earth. Usage of renewable resources becomes almost the only one alternative solution for the complex of gathered problems for living space long-term maintenance.

2.6. Fiber hydrophilicity/ hydrophobicity

Very important factor is fiber ability to absorb or remove water molecules. This characteristic is called hydrophilicity or hydrophobicity. If fibers absorb water it is called a hydrophile fiber and it has a set index – water absorption coefficient. As it is known from the experimental research, it is better if the fiber is more hydrophobe not hydrophile; otherwise it is needed to make additional treatment to divide absorbed water molecules. But it is known that almost all polymers are hydrophobe. It influences further composite extraction as fibers are different from their chemical structure. The main feature of the nature fibers structure is that they contain a lot of hydroxyl groups and therefore they absorb water molecules but in the structure of the unmodified polymer functional groups only some have hydroxyl groups.

Fiber drying before the further processing is very important factor because water molecules work on the fiber surface as dividing agent between the fiber and matrix surface. During the water steaming pores appear in the matrix. The influence of these both processes makes a big significance on mechanical qualities of the material. Therefore fiber drying needs to be done in vacuum at different temperatures.

Water absorption influence on polypropylene matrix composite material that is strengthen with hemp fibers, was researched accordingly to LVS EN ISO 62: 2008 standard. [11] Samples of composite materials were dried in the drying cupboard at the temperature of $105^{o}C$, and its keeping time was 48 hours. After the keeping time samples were taken out of the drying cupboard and put into exsiccator with the preciseness up to 0,1 mg to let them cool down to the room temperature.

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3. EXPERIMENT

3.1. The composite material

To create a composite material hemp type "Bialobrzeskie" were used that were cultivated in the Kraslava district in Latvia. (Figure 5) As L. Freivalde's research shows [12], this type is very suitable for creation of composite materials and also weather conditions in Latvia are appropriate for its' growth.

As composite material matrix polypropylene fibers „Fibre mesh 300", were used that are imported from England. [Figure 6] These fibers are already lengthened by 12 mm. In order to make the more even planking, lengthened fibers were rarefied to make the mono fiber planking out of fiber entirety.

Figure 5. Hemp fibres

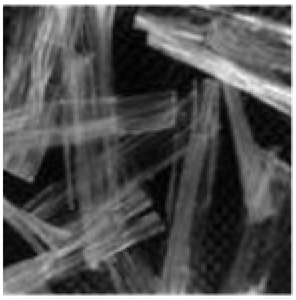

Figure 6. Fibers of polypropylene "FiberMesh 300"

Hemp fibers were schuched to clear out shives, separate long fibers from the short ones and get regular fiber planking. For the first samples of the experiment (parallel fiber orientation) long fibers were used that were lengthened by 260mm. Fiber length was measured by die size. For the creation of samples 50% and 70% fiber amount from the total sample weight was used. Before the creation of samples the fibers were dried in the drying cupboard (CHBC-45.4.54) at the temperature of 60^{o}C with the exposure time of 4 hours.

Since the process is happening in the fever heat and the polymer is melting, it is necessary to have aluminium foil plates that ensure homogeneous pressed composite surface and possibility to take out created composite from the termopress device more easily. Aluminium foil plates are cut in size of 265 x 265mm which is set by die size.

Aluminium foil, polypropylene fibers and hemp fibers were put in layers, making the composition of laminate type. Aluminium foil was put on both sides of the composite. [Figure 7]

Samples were created taking into account the prepared experiment plan at the beginning of the experiment. As unchangeable factors: weight - 14g, pressure – 7,66kg/cm^2, time - 20 min. were set up. As the changing factors were used proportion of materials in the samples (hemp fibers against polypropylene fibers) and temperature in which the samples were made- 170^{o}C or 190^{o}C. Size of the created sample was 260x260x0,65 mm. There were made also samples with shunted wattle-work 2D hemp fabric with similar density but different layout (Figure 8; 9; 10).

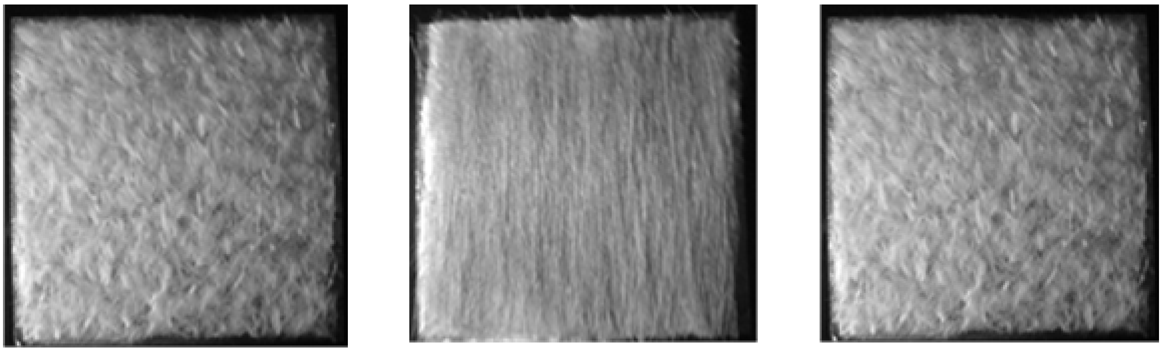

Figure 7. The principle of sample preparation

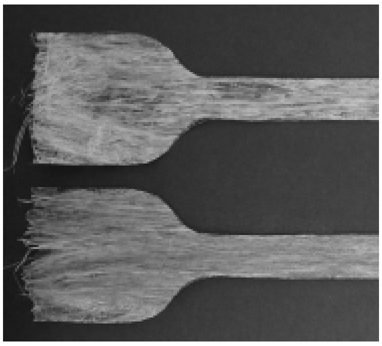

Figure 8. Hemp fiber test sample

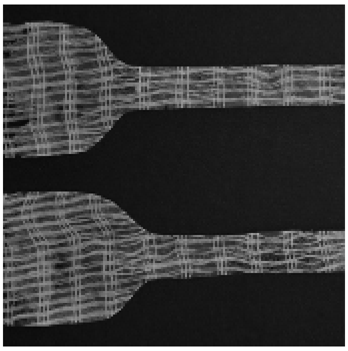

Figure 9. shunted wattle-work 2D hemp fabric test sample (M1)

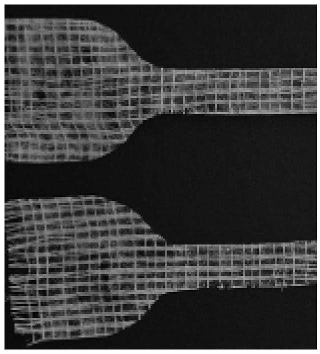

Figure 10. shunted wattle-work 2D hemp fabric test sample (M2)

3.2. Tensile testing

Tension tests for the composite material which is made from the polypropylene matrix and parallel long hemp fibers intensification were done with the ZWICK Z100 (maximum strength 100 KN) universal testing device using Tension 100kN.ZPV testing method. The maximum strength with the speed of 10 mm/min was used for tension verifications for sample and the length of sample was 90mm. Verification was done in the room temperature 22+/-2C^{o}. Number of verified samples was 16; 4 samples from each manufacturing set were tested and first results were obtained.

4. RESULTS AND DISCUSSION

4.1. Water absorption

Water amount absorption the composition was calculated in the following way: it was taken into account the sample weight before the drying and sample weight after the drying. For calculation the equation was used:

$$\Delta M(t) = \frac{m_t - m_o}{m_o} x\ 100$$

Where M(t) is humidity amount, m_o and m_t is sample weight after the drying and sample weight before the drying. Calculation was done for the samples that are developed at the temperature of 175°C and 190°C and 50/50 and 70/30 fiber and matrix proportions were used. (Table 4)

Nr. pk.	Creation T°C	Hemp fiber (%)	Polypropylene (%)	Weight before drying	Weight after drying	M(t) (%)
1	170	50	50	0,5421	0,5209	4,07
2	170	70	30	0,5742	0,5472	4,93
3	190	50	50	0,4858	0,4725	2,81
4	190	70	30	0,7392	0,7069	4,57

Table 4. Calculation of water absorption

4.2. Tensile properties

The degree of effectiveness of reinforcement can be characterized by the Young's modulus of the composites (Figure 11). As it is showed in the Figure 11, there have been made tensile tests for samples. The main results are that in general by lower temperature the tensile elongation is higher. Comparing the tensile elongation for samples of 50/50 proportion to samples of 70/30 proportion, we can conclude that the elongation ratio decreases very sharply for 50/50 samples by higher

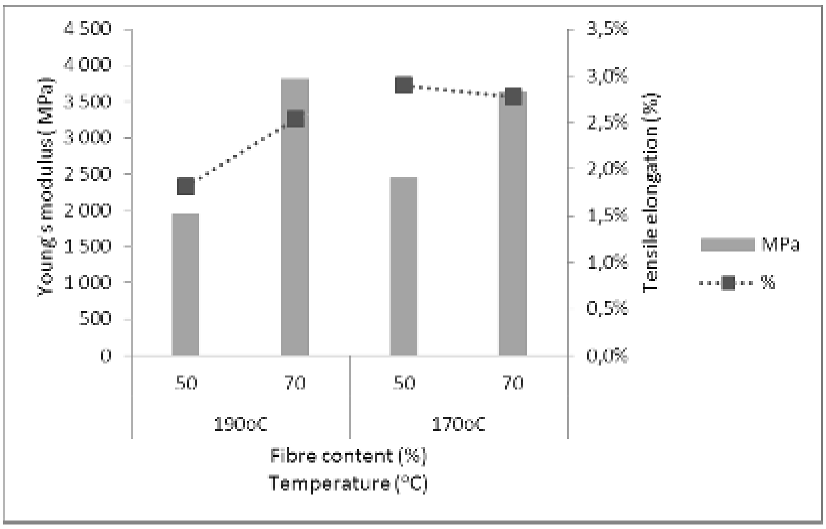

Figure 11. Young's modulus as function of fiber content, temperature and tensile elongation

temperature, but the elongation ratio is not so volatile for 70/30 proportion samples in both temperatures. Young's modulus is increasing along with the increase of fiber proportion in the sample.

Tensile strength for parallel fibers increase along with increasing hemp fiber proportion as can be seen in Figure 12. Maximum tensile strength by 170^0C is 53.58 (50/50 proportion) and 65.47 (70/30 proportion). Maximum tensile strength by 190^0C is 21.16 (50/50 proportion) and 47.4 (70/30 proportion). The tensile strength increases by lower temperature for 150% for 50/50 proportion and for 40% for 70/30 proportion that can be explained by fact that by 190^0C smoldering process of hemp fibers starts.

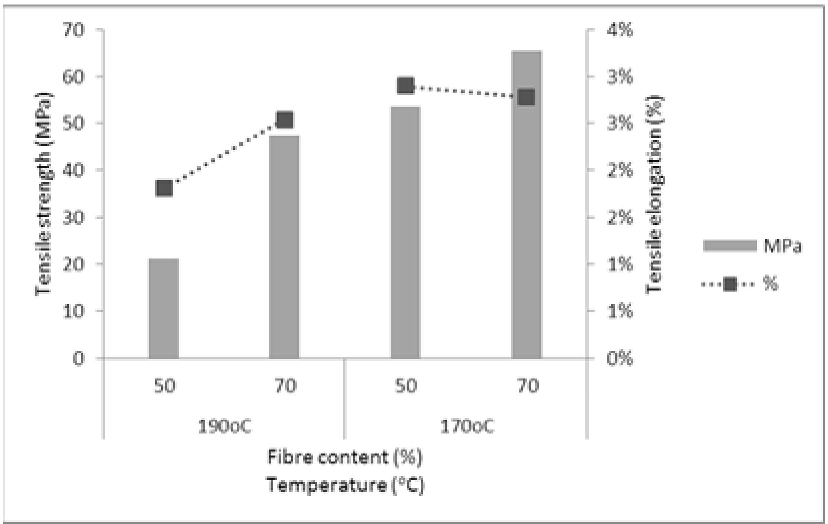

Figure 12. Tensile strength as function of fiber content, temperature and tensile elongation

In Figure 13 there is showed tensile strenght and elongation of two 2D fabrics in 170^0C and in two different proportion- 50% of fabrics and 70% of fabrics in sample. The main conclusions are that the material M2 has higher tensile strength. By increasing proportion of the fabrics increases also the tensile strength. Tensile elongation is higher for M1 by 50% proportion and M2 by 70% proportion.

In Figure 14 there is showe the comparison of 2D fabric composite's and hemp fiber composite's tensile strenght and tensile elongation. It is clear that the tensile elongation is much lower for the hemp fiber composites despite significantly higher tensile strength reaching 50-60 MPa compared to only about 20 MPa for 2D fabric composites. Tensile strength and elongation ratios are very similar for both- 50% proportion and 70% proportion samples.

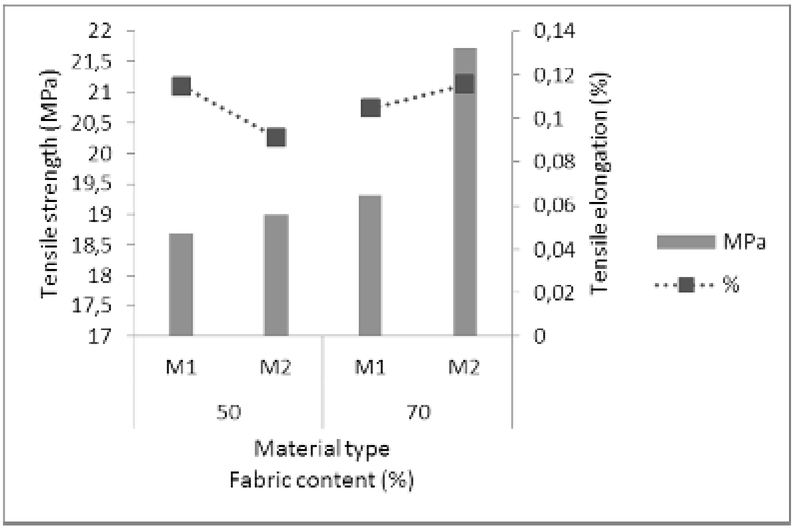

Figure 13. Tensile strength as function of two fabric content and tensile elongation

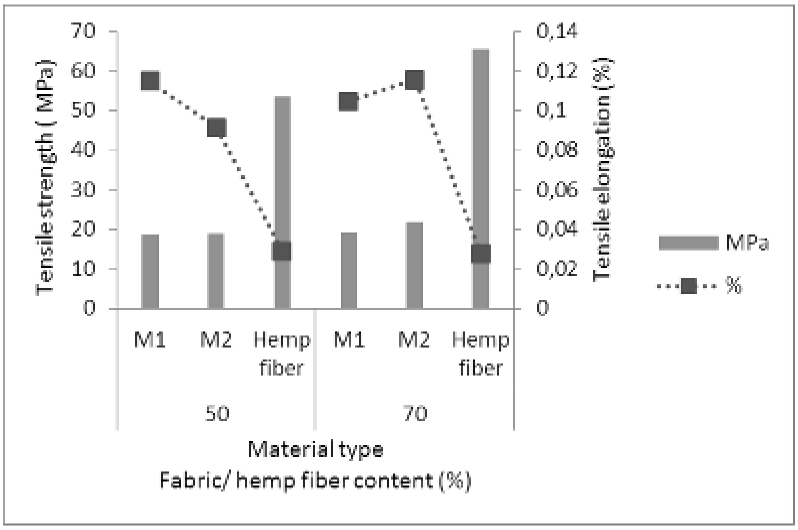

Figure 14. Tensile strength as function of two fabric content compared to hemp fibers and tensile elongation

5. CONCLUSION

In general it is proved that the composites made from natural fibers are also suitable in polypropylene matrixes. The composites reinforced with natural fibers will be used in different industries (transport, construction, packing etc.) due to fact that such materials are environmentally friendly and recyclable.

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These polypropylene matrixed reinforced with hemp fibers are partly biodegradable, but the highest challenge in the future will be to create fully biodegradable composites with PLA or starch matrix.

In this work there was created a new environmentally friendly material using hemp fibers. The tensile strength and elongation were tested in two different temperatures- 170^0C and 190^0C. It was investigated that tensile strength for parallel fibers increase along with increasing hemp fiber proportion but by lower temperature the tensile elongation is higher.

The water absorption for samples prepared in 170^0C is higher compared to samples prepared in 190^0C.

There were also made experiments comparing 2D fabric composite's and hemp fiber composite's tensile strenght and tensile elongation. It is clear that the tensile elongation is much lower for the hemp fiber composites despite significantly higher tensile strength reaching 50-60 MPa compared to only about 20 MPa for 2D fabric composites.

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