Mechanical Properties of Polypropylene Modified with Different Treated Hemp Fibers

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Polymer composites from polypropylene (PP) and treated and untreated hemp fibers (HF) were prepared using a twin screw extruder and separated feeding ports. Both treated and untreated HF show reinforcing effect in PP composites but the treatments applied to HF accentuate this effect. An increase with 78 % of tensile strength and with 61 % of Young's modulus was obtained with untreated fibers and double tensile strength and modulus when using treated HF. Aminosilane treatment of HF was the most efficient, leading to simultaneous improvement of tensile properties and impact strength of PP composites.

Keywords: hemp fibers, mechanical properties, twin screw extruder, polymer composites

The shift to more environmentally friendly materials for different industrial fields is an obvious trend in the last decade. The use of natural fibers in thermoplastic composites instead of glass or carbon fibers is considered a promising solution from both economical and environmental reasons. Natural fibers have many advantages compared to traditional glass fibers, they are cheap, biodegradable, have good mechanical properties and low density and also determine reduced tool wear and respiratory or dermal irritation when they are used as reinforcements for thermoplastic polymers [1-7]. Natural fibers are obtained from renewable resources that can be grown within a short period of time and their supply for polymer composites can be unlimited as compared with glass and carbon fibers. Natural fibers such as hemp have been identified as attractive reinforcements for polypropylene (PP) for automotive industry [8-9]. However, several problems related to the incompatibility between the hydrophilic HF and the hydrophobic PP matrix which lead to increased segregation of HF during processing and also the poor resistance of HF to moisture, limit the use of HF as reinforcements in PP composites. To overcome these drawbacks, several solutions have been proposed, that fall into two main categories: novel or improved processing techniques and physical or chemical modification of HF and/or PP matrix [1-2, 10-12]. Most of the research work on PP/HF composites is focused on the last solution. Different compatibilizers and coupling agents were tested to improve HF/PP interface, to enhance the mechanical properties of resultant composites. Among compatibilizers, maleated polypropylene and silanes are by far the most used among coupling agents. A recent review on silane coupling agents used for natural fiber/polymer composites shows the mechanism of silane action at the surface of natural fiber and the conditions that must be ensured to achieve maximum efficiency of the treatment [1]. As a general feature, silanes are hydrolyzed forming silanol groups and then condensed on the fiber surface in a sol–gel process. The hydrogen bonds formed between OH groups of natural fibers and silanol groups can be converted into covalent bonds by heating the treated fibers at a temperature generally higher than 100 °C. The silane functionality controls the fiber/matrix adhesion, chemical bonding between the organofunctionality of silane and polymer matrix leading to the highest efficiency in improving the interfacial adhesion. As a result, the mechanical properties of composites are highly enhanced, direct correlation between interface properties and mechanical behavior being already established [1, 13]. Less literature is focused on the improvement of the processing technique and, much less on the simultaneous influence of the both fiber treatment and processing procedures. Therefore, this paper presents the combined influence of different treatments of HF and improved processing technique using a twin screw extruder and separated feeding ports for HF and PP. An aminosilane, polyvinyl acetate and an acrylic finishing agent were used for HF treatment. The improved adhesion at fiber – matrix interface was evaluated by mechanical characterization (tensile properties, impact strength and hardness) and rheological behaviour.

Experimental part

Materials and methods

A polypropylene homopolymer Moplen HP 500 N (PP), with the characteristics shown in table 1 was used as

Table 1
POLYPROPYLENE CHARACTERISTICS

Properties	Method	Value
Density, g/cm^3	ISO 1183	0,90
Melt flow index, (230ºC/2.16 kg), g/10 min	ISO1133	12
Modulus of elasticity, MPa	ISO 527	1550
Tensile strength at yield, MPa	ISO 527	35
Charpy impact strength (unnotched specimens), kJ/m^2	ISO 179	110

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Fig. 1. Short cut AS treated hemp fibers (AS-HF); inset - Granules of PP with AS-HF obtained on the twin screw extruder

polymer matrix. Short cut hemp fibers used as reinforcement in polypropylene were obtained at National R&D Institute for Textile and Leather as described in the following paragraph. 3-aminopropyltriethoxysilane was supplied by Sigma Aldrich, polyvinyl acetate by Rasnov Romania and the acrylic finishing agent (Crilotan) by Bozeto Giovani S.P.A., Italy and they were used without any purification for the surface modification of the fibers.

Preparation of short cut hemp fibers

The bundles of hemp fibers were chemically cleaned by alkaline boiling for one hour using soda ash, caustic soda, trisodium phosphate and wetting agent. Several cycles of rinsing with water and centrifugation for 5 min were applied for bringing the *p*H of hemp fibers to a value close to 7 and maximum 50 % water content. Hemp fibers (HF) were then dried in a circulating air oven at a temperature of 60 – 70°C for about 3 h and cut at a size of fibers of 4 - 6 mm.

Part of the cleaned fibers was treated for the improvement of polypropylene – HF adhesion with three types of hydrophobising agents: an aminosilane (AS), polyvinyl acetate (VA) and an acrylic finishing agent (C). For the treatment with AS, HF were added in a 90/10 ethanol/water mixture containing 10% AS and the suspension was stirred for 2 h at room temperature and then heated for 1 h at 110C. The VA and C treatments consisted of the following steps: cold impregnation with VA or C 60 g/l for 20 min, centrifugation till ~ 50 % water content, drying and self-reticulation at 105°C. Treated hemp fibers (AS-HF, VA-HF and C-HF, respectively) were cut at a size of fibers of 4 - 6 mm. AS treated hemp fibers are shown in figure 1.

Preparation and characterization of polypropylene – hemp fibers composites

Treated and untreated hemp fibers were dried in a circulating air oven at a temperature of 60 – 70°C for about 3 h before the preparation of composites. A co-rotating twin screw extruder Leistritz 30…34, equipped with water cooling bath and pelletizer (Germany) was used for the preparation of composites. PP granules and hemp fibers (HF, VA-HF, C-HF and AS-HF) were loaded in the extruder through different feeding ports (fig. 2).

PP granules were fed by a screw feeder (two horizontal screws) at controlled rates and the fibers by a vertical screw feeder located at the middle of the extruder cylinder. The

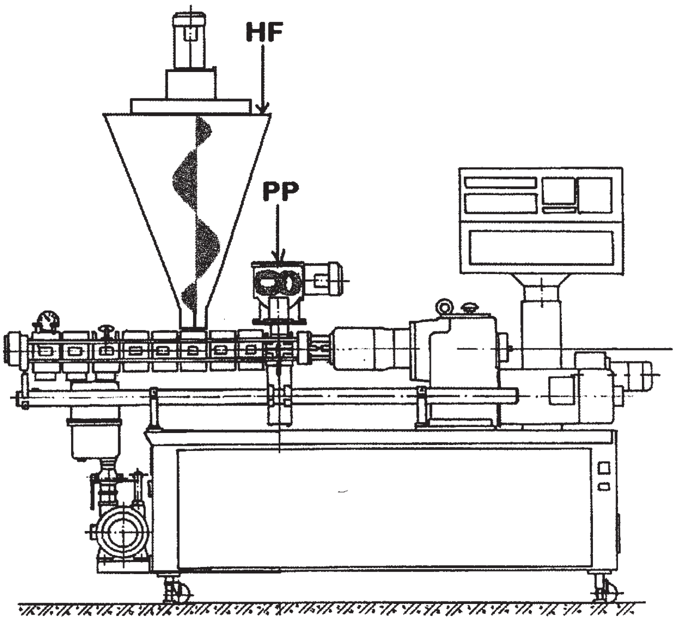


Fig. 2. Twin screw extruder with the two ports for separate feeding of granules and fibers

rate of the two feeders was set so that a concentration of 25 wt% of fibers in the composites to be reached.

The composites in fibrous form were cooled in the water bath and fed to a pelletizer to get pellets with the size of 2 x 4 mm (fig. 1 - inset). Dog-bone shaped samples used for the mechanical characterization of composites were obtained by injection on an Engel 40/25 injection machine, die temperature of 200°C, pressure of 1400 daN/cm^2. Tensile properties were determined using Instron 3382 Testing Machine (Great Britain) at room temperature with a crosshead speed of 50 mm/min. Five specimens IB type according to ISO 527 were tested for each sample. Shore D hardness was determined on 4 mm thick specimens according to ISO 868 using a Zwick penetrometer (Germany). Izod impact strength was determined on notched specimens according to ISO 180 using a Zwick Impact Tester HIT5.5P (Germany).

Characterization of melt processing properties was done by melt flow index (MFI) determination using a plastometer capillary rheometer (LMI 4003 Melt Indexer from Dynisco, USA). Although the MFI is a simple single point method that neglects the complex time dependence of rheological properties, it is widely used to characterize the rheological properties of polymers and composites [14]. MFI of PP and PP containing hemp fibers was determined according to ISO1133.

The composites were denoted as follows: PP/HF for the composite containing untreated fibers, PP/AS-HF, PP/VA-HF and PP/C-HF for composites containing AS-, VA- and C- treated fibers, respectively.

Results and discussions

Establishment of process parameters

The most suited technology for the preparation of thermoplastic polymers/natural fibers composites is by extrusion using a twin screw extruder. However, the dry mixing of short cut natural fibers with the granules of the thermoplastic polymer prior to extrusion is a difficult operation. Room temperature mixing of the two components was tried using a Trusioma type intensive mixer (rotor speed 500 - 1500 min^{-1}) and a Turbula type mixer with complex rotation on three directions. None of these methods led to a good homogenization of the two components. Natural fibers remained in great amount at

Extrusion parameters	Values
Temperature of the extruder zones, °C	190; 200;215; 195; 200; 200; 200; 200; 200
Temperature of the die, °C	200
Temperature (in material), °C	190
Screws rotation speed, min^{-1}	40
Screws rotation speed at the first feeder (PP granules), min^{-1}	50
Screw rotation speed at the second feeder (hemp fibers), min^{-1}	20

Table 2
EXTRUSION PARAMETERS FOR PP/HEMP FIBERS COMPOSITE PREPARATION

Properties	PP	PP/HF	PP/C-HF	PP/VA-HF	PP/AS-HF
Shore D Hardness, ^{0}Sh	64	70	70	72	72
Melt flow index (230 °C, 2.16 kg), g/10 min.	12.2	25.1	7.8	17.0	18.9

Table 3
SHORE HARDNESS AND MELT FLOW INDEX OF PP AND COMPOSITES

the surface of the mixture because of their low bulk density and different aspect, no matter what rotor speed and mixing time were used. A third component with high surface tension was also used in order to improve the mixing efficiency. The homogenization was better but domains with the same material type were still visible. Moreover, the components separated when feeding the extruder. Therefore, separated feeding of the two components was tried using two different feeding systems, specific to the granules and natural fibers, respectively: a feeding system with horizontal screws that ensure constant and adjustable feeding of polymer granules and a feeding system with vertical screw that ensure the force feeding of natural fibers.

For establishing the speed of each feeding system, so that a certain concentration of HF to be reached in the final composite, neat PP was extruded on the co-rotating twin-screw extruder and the optimal parameters were established (temperature on the ten zones of extruder, speed of the extruder screws and of the feeding system). The temperature of the extruder zones was adjusted to the values specified in table 2 while the temperature of the die was 200°C.

The output for neat PP and the quantity of natural fibers at different rotor speeds of the second feeding system were also established. From these data the speed of the second feeding system was calculated so that a concentration of 25 wt% HF to be found in the composite material. The composite obtained using these parameters was analyzed and the concentration of natural fibers was determined by boiling in decalin for about 1 h at 140 °C for PP solubilization and HF separation by filtration. Approximately 25 % HF was found in the final composite.

Mechanical and rheological characteristics of composites

Tensile properties of neat PP and composites are shown in figure 3a-c.

Several interesting aspects can be drawn from these figures. First, adding untreated HF led to an increase with 78 % of tensile strength and with 61 % of Young's modulus and to a dramatic decrease of elongation at break, an important reinforcing effect being thus signaled. Adding treated HF led to further improvement of mechanical properties, the efficiency of the reinforcing effect depending on the type of the treatment.

The most important improvement of the tensile modulus (2.2 times) was noticed when C-HF were used as reinforcement in PP but the overall improvement of mechanical properties was observed for PP reinforced with AS-HF: tensile strength increased by 2.2 times, tensile modulus doubled and impact strength increased by 2.5 times as compared to neat PP (fig. 3d). Aminosilane treatment of HF seems to be the most efficient treatment leading not only to an improvement of tensile properties but also to an important increase of the impact strength. An improvement of the impact response was also reported for non-woven hemp fiber reinforced unsaturated polyester composite [15].

Shore hardness (table 3) was higher for the composites as compared with neat PP but the differences between composites containing HF with different treatments were small.

Application of supplementary treatments to HF led to significant improvement of all mechanical properties (fig. 2a-d) which emphasized the improvement of interfacial properties by the increase of adhesion between fibers and polymer matrix [16-17].

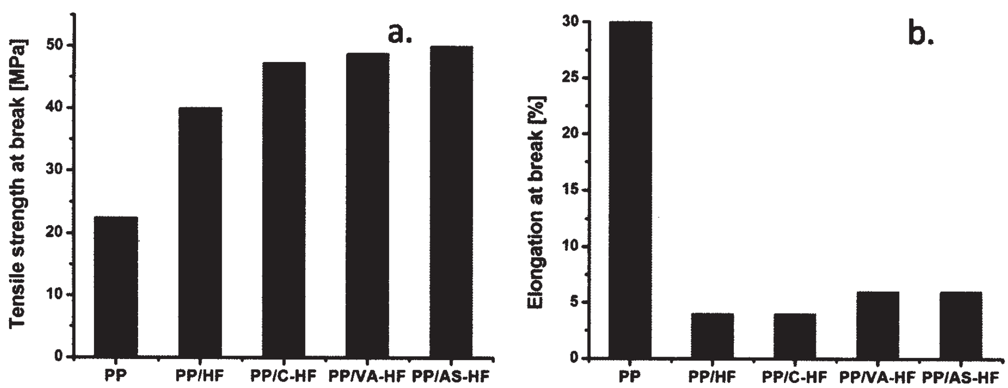
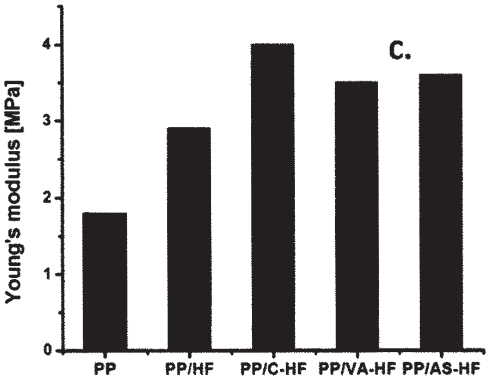


Fig. 3 (a, b). Mechanical properties of PP and PP composites with treated and un-treated HF:
a. Tensile strength at break;
b. Elongation at break



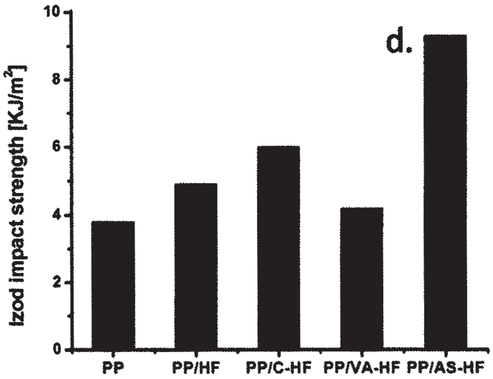


Fig. 3.(c, d). Mechanical properties of PP and PP composites with treated and un-treated HF: c. Young's modulus; d. Izod impact strength

Melt flow index of PP and composites was shown in table 3. The MFI values for the composites with treated HF were lower than for the composite with untreated fibers revealing the higher reinforcing effect and the reduced influence of treated HF on the thermal stability of PP. Thermal analysis of samples will be undertaken to determine the influence of treated and untreated HF on the melting behaviour and stability of PP.

Conclusions

Different treatments were applied to HF and the efficiency of treated HF as reinforcement in PP was evaluated in comparison with untreated HF. Polymer composites based on PP and treated or untreated HF were prepared using a twin screw extruder and separated feeding ports with two different feeding systems, specific to granules and natural fibers, respectively. An increase with 78 % of tensile strength and with 61 % of Young's modulus was obtained with untreated fibers. Further improvement of tensile strength and modulus, of over 100 %, was obtained for PP composites with treated HF. Aminosilane treatment of HF was the most efficient, leading to simultaneous improvement of tensile strength and modulus and also of impact strength of PP composites.

References

1. XIE, Y., HILL, C.A.S., XIAO, Z., MILITZ, H., MAI, C., Compos. Part A, **41**, nr. 7, 2010, p. 806.
2. RACHINI, A., LE TROEDEC, M., PEYRATOUT, C., SMITH, A., J. Appl. Polym. Sci., **123** nr. 1, 2012, p. 601.
3. PANAITESCU, D.M., IORGA, M.D., SERBAN, S., FRONE, A.N., Mat. Plast., **47**, nr. 1, 2010, p. 1.
4. DAI, D., FAN, M., Mater. Sci. Appl., **1**, nr. 6, 2010, p.336.
5. TAJVIDI, M., MOTIE, N., RASSAM, G., FALK, R.H., FELTON, C., J. Reinf. Plast. Compos., **29**, nr. 5, 2010, p. 664.
6. LI, H., SAIN, M.M., Polym.-Plast. Technol. Eng., **42**, nr. 5, 2003, p. 853.
7. GOUTIANOS, S., PEIJS, T., NYSTROM, B., SKRIFVARS, M., Appl Compos Mater., **13**, nr. 4, 2006, p. 199.
8. KORONIS, G., SILVA, A., FONTUL, M., Compos. Part B, **44,** nr. 1, 2013, p. 120.
9. RIEDEL, U., NICKEL, J., Applications of Natural Fibre Composites for Constructive Parts in Aerospace, Automobiles and Other Areas, In: Biopolymers General Aspects and Special Applications, 10. Wiley-VCH, 2002, p. 1-28.
10. PRACELLA, M., CHIONNA, D., ANGUILLESI, I., KULINSKI, Z., PIORKOWSKA, E., Compos. Sci. Technol., **66,** nr. 13, 2006, p. 2218.
11. TSERKI, V., ZAFEIROPOULOS, N.E., SIMON, F., PANAYIOTOU, C., Compos. Part A, **36**, nr. 8, 2005, p. 1110.
12. HO, M-P., WANG, H., LEE, J-H., HO, C-K., LAU, K-T., LENG, J., HUI, D., Compos. Part B, **43**, nr. 8, 2012, p. 3549.
13. KU, H., WANG, H., PATTARACHAIYAKOOP, N., TRADA, M., Compos. Part B, **42**, nr. 4, 2011, p. 856.
14. GARCIA-FRANCO, C.A., MEAD, D.W., Rheol. Acta, **38**, nr. 1, 1999, p. 34.
16. DHAKAL, H.N., ZHANG, Z.Y., RICHARDSON, M.O.W., ERRAJHI, O.A.Z., Compos. Struct., **81**, nr. 4, 2007, p. 559.
16. YAN, Z., ZHANG, J., ZHANG, H., WANG, H., Adv. Mater. Sci. Eng., 2013, Article ID 941617, 7 pages.
17. KIM, J-K., MAI, Y-W., Compos. Sci. Technol., **41**, nr. 4, 1991, p. 333

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