MECHANICAL PROPERTIES OF HYBRID COMPOSITES BASED ON POLYPROPYLENE MATRIX

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The paper is focused on the analyses of the mechanical and physical properties of the hybrid composite systems based on the polypropylene matrix with implemented reinforcing cellulose fibres. The polymer phase of this conventional composites is furthermore modified by physical blowing agents, which are utilized for the formation of light microcellular structures. Interactions of all the components of these hybrid composites are evaluated in terms of density change, impact resistance, bending and tensile properties. Complying with the assumption closed pores generally decreased mechanical properties of the multiphase composite systems. The reduce of mechanical properties induced by presence of the microcellular structure was more significant with increasing level of filling by reinforcing particles.

KEYWORDS

cellulose fibres, polypropylene, hybrid composites, physical foaming agents, mechanical properties

1 INTRODUCTION

Natural cellulose fibres are used in the polymeric matrix primarily as reinforcing fillers. From environmental and economic point of view the composites with natural filler have many other benefits. The fibres are obtained from renewable sources and replace the synthetic matrix. Implementation of cellulosic fibres into the polymer matrix in turn reduces the overall density of the composite systems (if the fillers have a lower density than the matrix), reduces the material costs and in general positively modifies the mechanical properties. Other currently widespread modification of polymer matrix includes reducing its density using chemical or physical blowing agents. The combination of these modifications allows the formation of a completely new generation of hybrid multifunctional composite materials with unique properties [Bledzki 2006, Faruk 2007].

2 POLYMER COMPOSITES

Composites are heterogeneous materials which consist of two or more phases in the macroscale. These phases mutually significantly differ in their mechanical, physical and chemical properties. From the alloys the composites differ mainly in the preparation process, because the creation of the composite materials necessitates mechanical mixing of the components to achieve a homogeneous distribution, while the alloys are formed by diffusion processes [Shalin 1995, Taj 2007]. The most important reason for continuous development is called synergism that is characteristic for these materials, which means that the properties of the resulting composites are even better than only adding the properties of individual components together. Synergism leads for example to obtain qualitatively new properties of composite materials. The processes at the interface between the two (or more) phases are reason for such improvement of properties and sometimes hardly predictable behaviour of composites. [Mohanty 2005]

2.1 Matrix

The main role of polymer matrix as a basic component in reinforced composite is tension transfer to the fibres, fibres protection from environmental influences and their mechanical abrasion during processing. Good process ability, corrosion resistance and shock absorption are the most advantageous properties of plastics and as a continuous phase matrix gives the composite its characteristic molecular weight, crystallinity and controls the interactions with the filler surface. With increasing molecular weight of the matrix the viscosity of the polymer melt increases and mechanical properties, thermal and chemical stability are improved. [Xanthos 2009, Rosato 2004]

2.2 Fillers

Additives for polymer composites are of natural or synthetic origin. In the 21st century, however, the need to stop wasting natural resources is an actual topic and that is way the synthetic components derived from the petroleum should be replaced by materials from renewable sources. [Shalin 1995, Blackburn 2005] Natural fillers do not reach such a high reinforcing effect in comparison to synthetic fibres, but they are used primarily to reduce the price of the final composites. Therefore, they are added to the polymer matrix in a large amount to reduce weight of the composite system and the volume of synthetic components. [Xanthos 2009, Rothon 2001] The fillers affect the final properties of the composite systems by their nature, geometry, distribution of shapes and sizes, concentration, surface profile and their physical, chemical and mechanical properties. [Müssig 2010, Shalin 1995] Materials applied as fillers must meet the requirements such as heat stability, chemical resistance, minimal toxicity, recyclability, low hardness (minimal abrasion of processing equipment), good availability, wettability and compatibility with the matrix etc. Implementation of natural fibres into the polymer matrix during compounding is a challenging process. The fibres flocculate into bundles (agglomerates) and the homogenous distribution could be problematic. The pores creating microcellular structure reduce the contact area between the fibres and the matrix and thereby decrease reinforcing effect (reduced tension transfer from the matrix to the fibres). [Taj 2007, Xanthos 2009]

2.2.1 Cellulose

Cellulose belongs among the most widely spread substances in the world that is not only an essential structural component of plants, but it can also be produced by bacteria or fungi. [Lewin 2007] Availability, relatively low cost and especially degradability are its main advantages. Glucose monomers are the building unit of the cellulose that are included among semi-crystalline polymers. For industrial purposes the cellulose is derived from wood and cotton. Mechanical and physical properties of the cellulose depends mainly on the polymerization degree and are strongly affected by its hydrophobic character. [Kalia 2011]

2.3 Interphase

Effective contact among all the systems is critical for creation

compact composite material. Quality interphase is essential especially for load transfer and affects the physical and processing properties. The behaviour at the interphase is affected by many factors such as the wettability of the reinforcement by the molten matrix, the melt viscosity and the surface profile of the reinforcement. From the physical point of view thermal expansion of all the phases is also very important. Mutual interactions are based on the nature of bonds between matrix and reinforcement. Mechanical bonds are the weakest type of connection and are dominant at the interphase of inert phases. Physical bonds are probably the most common bonding type and the connections of two systems is based primarily on the interaction between two dipoles, or the forces are transmitted through the Van der Waals bonding. The strongest connection is provided by the chemical bonds. [Taj 2007] Considering the physical and chemical actions among all phases the interface is not only the contact zone, but includes also the area that is deformed by thermal expansion of individual phases caused by their different stiffness and thermal expansion coefficient. From the chemical point of view, the interface has a composition identical to the matrix composition (if the adhesion is not enhanced using chemical compatibilizers or other type of surface treatment), but from the morphological point of view the interphase has completely different structure (lower mobility of the macromolecular segments in this layer). [Rothon 2001, Han 2007]

2.4 Foaming (blowing) agents

Microcellular structures can be created basically in two different ways (using physical or chemical foaming agents). Chemical foaming agents are the solids, that are decomposed at specific temperature (processing temperature of the polymer) into low molecular substances creating the closed pores. Physical foaming agents are compounds that liberate gases as a result of physical processes. The final selection of the physical foaming agent is based on the type of desired microcellular structure and costs of the foaming process. The applicable foaming agents were limited by the Montreal Protocol. The exploitation of the substances with high ozone depletion potential (ODP) and global warming potential (GWP) was prohibited. Currently the most widespread physical foaming agents are nitrogen and carbon dioxide for their environmentally friendly character. These inert gases are preferred for good solubility in the polymer matrix, high foaming potential, nonflammability, nontoxicity, no residues liberated during the foaming process etc. [Faruk 2007, Lee 2005]

2.4.1 Foaming process

MuCell technology commercialized by Trexel is one of the special moulding techniques producing microcellular foams. The injection of inert gas (nitrogen or CO2) in the form of supercritical fluids (SCF) into the thermoplastic melt in the plasticization section of the barrel is the essence of this process. The microcellular structure with closed pores is created after the injecting of the melt into the mould cavity and the pressure drop. The structure is usually fixed by cooling the materials below the melting point and the pores reach size from 5 to 50 microns. [Xu 2001]

Generally, foaming injection moulding achieves not only product weight savings but also increased melt flowability, smaller shot size (compensation of the holding phase), lower injection pressures, faster cycle times, and better dimensional stability. [Jacobsen 2000, Moore 2001]

3 EXPERIMENT PROCEDURE

The submitted study involves analyses of physical and mechanical properties performed by multiphase systems composed of a polypropylene matrix and natural cellulose-based fibres. The conventional injection moulding and SCF (nitrogen) assisted injection moulding which results in formation of a specific microcellular structure were used for production of test specimens.

3.1 Material

Matrix based on homopolymer with the trade name PP SABIC 595A was the basic phase of the composite system. This polypropylene has excellent flow properties that are preferred for the production of reinforced composite systems. High rigidity and good processing character are beneficial especially for injection moulding of parts in automotive industry. The prime properties of the polymer matrix were modified by cellulose fibres. D-glucose was the basic building unit of the processed cellulose chain. The composites involved into this study contained 10 wt. %, 20 wt. % and 30 wt. % of cellulosic fibres. The fibre surfaces were modified by coupling agent based on organosilanes (introduced by Dow Corning).

3.2 Composite preparation

Composite systems were prepared using strand granulation. The natural fibres were milled on the knife cutting mill Retsch SM 300 with cyclone separator and the sieve with trapezoidal holes with dimension of 0.75 mm (with length distribution from 0.5 mm to 2 mm). As a last step of the preparation the natural fibres were dried in the hot oven VENTICELL with forced air circulation which ensured homogeneous temperature distribution (80°C for 4 hours). Palletisation was realized using the line ZAMAK EEA - 2x130di equipped with twin screw extruder, the calibrated die head, water bath, guiding rollers, air knife and mill feeder.

3.3 Specimens moulding

From the prepared pellets the multipurpose test specimen (type A, complying with international standard EN ISO 3167) were moulded. These specimens are designed primarily for evaluation of the tensile properties. The metering part zone of these specimens can be used for the analyzes of other mechanical properties (in this case bending and impact characteristic). For each analysis ten specimens were prepared.

3.3.1 Conventional injection moulding

The specimens were moulded in accordance with international standards EN ISO 294-1 and EN ISO 1873-2. Specimens produced by conventional injection moulding method was performed using Aurburg 270 S 400-100. Technological parameters are shown in table 1.

Parameter	Unit	Value
Melt temperature	°C	200
Mould temperature	°C	40
Cycle time	s	60
Holding time	s	40
Holding pressure	MPa	40
Shot size	cm³	40
Switchover point	cm³	16
Injection rate	cm³/s	30

Table 1. Basic technological parameters for injection moulding

3.3.2 MuCell technology

Production of test specimens with microcellular structure was performed on the machine Arburg Allrounder 470S 1000-400, which is equipped with modified injection unit (for MuCell technology with relevant peripherals). When plasticizing melt, the supercritical fluid (nitrogen) was injected in the front of screw. The intensive mixing was achieved by a special design of the screw that ensured homogenous distribution of the SCF in the entire volume of the melt. The technological parameters are listed in table 2.

Parameter	Unit	Value
Melt temperature	°C	200
Mould temperature	°C	40
Cycle time	s	60
Holding time	s	40
Holding pressure	MPa	40
Shot size	cm^3	40
Switchover point	cm^3	16
Injection rate	cm^3/s	30
SCF mass flow rate	kg/h	0,45
SCF dosing time	s	6
SCF injection pressure	MPa	20,5

Table 2. Basic technological parameters for Mucell technology

4   MEASUREMENT AND DISCUSSION

The analyses of multiphase systems were based on the evaluation of density change and its impact on bending and tensile properties and impact resistance.

4.1 Density analysis

The density of the specimens was determined complying with international standard EN ISO 1183-1 (immersion method).

As the immersion fluid methanol having a density of 0.791 g/cm³ at 23 °C was used for specimens made by conventional injection moulding. For microcellular systems liquid with lower density was employed. For this purpose petroleum ether having density of 0.650 g/cm³ at 23°C was employed. The average values with standard deviations are reported in table 3.

Material	Fibres concentration [%]	Density [g/cm3]	Standard deviation [g/cm3]
PP	x	0,906	±0,001
PP+cell. fibres	10	0,938	±0,004
	20	0,978	±0,004
	30	1,023	±0,003
PP+cell. fibres+ nitrogen	10	0,739	±0,01
	20	0,773	±0,011
	30	0,81	±0,009

Table 3. Impact of cellulose fibres presence and microcellular structure on density of final composites

The measured values clearly indicated that the cellulose fibres increased the density of the composite systems based on polypropylene matrix. The Fig. 1 shows the linear increase in density by 4.6% per each added 10 wt. % of cellulosic fibres. The overall density of lightweight systems exhibited similar tendencies. The microcellular structure, however, caused a decrease in density of all composite systems by 21%.
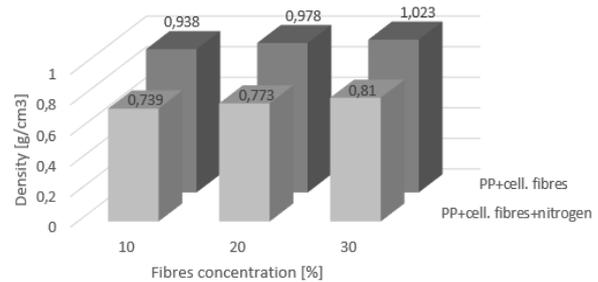
Figure 1. Comparison of measured densities

4.2 Impact strength analysis

Measurement the Charpy impact strength was carried out under standard conditions according to 179-1 / 1eU (impact on the narrower side of the specimen) using testing device Ceast Resil 5.5. The specimens had dimensions of 80 x 10 x 4 mm. To determine the impact strength of specimens made by conventional injection moulding hammer with a nominal energy of 5 J was used and lightweight specimens were broken using hammer with nominal energy of 2 J, so that the specimen resistance ranged between 10% and 80% of the hammer potential energy. The results are shown in the table 4.

Material	Fibres concentration [%]	Impact resistance [kJg/m2]	Standard deviation [kJ/m2]
PP	x	79,2	±1,5
PP+cell. fibres	10	31,9	±2
	20	27,8	±3,7
	30	25,4	±2,1
PP+cell. fibres+ nitrogen	10	16,1	±2,9
	20	15,7	±2,6
	30	15,3	±2,3

Table 4. Impact of cellulose fibres presence and microcellular structure on impact strength of final composites

Fibre reinforcement of PP matrix resulted in a reduction in impact resistance. The polymeric matrix reached values of 79.2 ± 1.5 kJ/m², whereas the presence of natural fibres decreased impact strength by more than a half of the initial value for all systems, as shown in Fig. 2. The highest brittleness was measured during analyses of systems reinforced with 30 wt. % of natural fibres (25.4 ± 3.7 kJ/m²). The porous structure of lightweight specimens reduced the impact resistance up to 20% of the value achieved by pure PP.
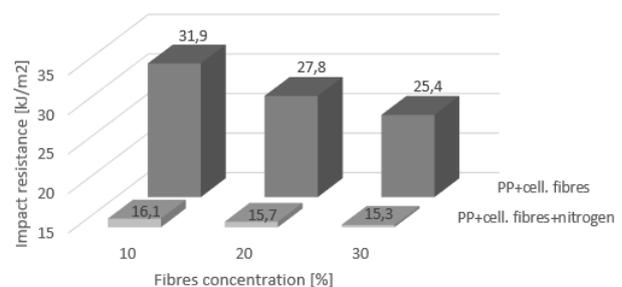
Figure 2. Comparison of reached impact resistances

4.3 Bending properties analysis

Bending tests revealed the flexural strength and flexural modulus of elasticity according to EN ISO 178 (three-point

bending). Characteristics were measured on specimens with dimensions 80 x 10 x 4 mm using a Hounsfield H10KT with the range of the sensor head up to 500 N. The testing speed was 2 mm/min.

The measured values captured in table 5 and 6 indicate positive influence of the presence of reinforcing fibres on flexural strength and flexural modulus. The polypropylene matrix reached the value of 48.3 ± 1.7 MPa when measured flexural strength and 1485 ± 75 MPa when measured the flexural modulus. With increasing concentrations of the reinforcing fibres the flexural strength increased up to 63.7 ± 0.5 MPa at the concentration of 30 wt. %. The increase in flexural modulus was even more pronounced at the highest concentrations and the composites reached the value of 2635 ± 68 MPa. Microcellular structure again eliminated the reinforcing effect of the natural fibres, see Fig. 3. Bending strength decreased slightly with increasing concentration of natural fibres, but the resulting values were comparable to those achieved with pure matrix (min. value of 46 ± 1.6 MPa). Bending modulus was conversely growing even in the presence of pores. The maximum value was reached by systems with the highest level of reinforcing fillers (2394 ± 84 MPa).

Material	Fibres concentration [%]	Flexular strength [MPa]	Standard deviation [MPa]
PP	x	48,3	±0,3
PP+cell. fibres	10	57,9	±1,1
	20	59,9	±0,9
	30	63,7	±0,5
PP+cell. fibres+ nitrogen	10	48,3	±1,7
	20	47,7	±0,9
	30	46	±1,6

Table 5. Impact of cellulose fibres presence and microcellular structure on flexural strength of final composites

Material	Fibres concentration [%]	Flexular modulus of elasticity [MPa]	Standard deviation [MPa]
PP	x	1485	±75
PP+cell. fibres	10	2205	±102
	20	2385	±96
	30	2635	±68
PP+cell. fibres+ nitrogen	10	2140	±82
	20	2291	±51
	30	2394	±84

Table 6. Impact of cellulose fibres presence and microcellular structure on flexural moduli of final composites
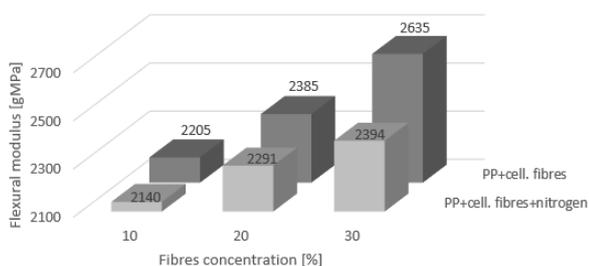
Figure 3: Comparison of reached flexural moduli

4.4 Tensile properties analysis

Measurement of the tensile properties was performed on the tensile apparatus TiraTest 2300 with the sensor head used up to 100 kN, respectively 10 kN. Testing speed of 5 mm / min was used in accordance with standard ČSN EN ISO 1873-2. Measurement of tensile modulus was carried out at the testing speed of 1 mm / min.

Material	Fibres concentration [%]	Tensile modulus of elasticity [MPa]	Standard deviation [MPa]
PP	x	1635	±61
PP+cell. fibres	10	2073	±115
	20	2401	±83
	30	2752	±87
PP+cell. fibres+ nitrogen	10	1657	±11
	20	1745	±69
	30	1746	±51

Table 7. Impact of cellulose fibres presence and microcellular structure on tensile moduli of final composites

Material	Fibres concentration [%]	Tensile strength [MPa]	Standard deviation [MPa]
PP	x	32,4	±0,1
PP+cell. fibres	10	33,8	±0,6
	20	34,9	±0,6
	30	37,3	±0,8
PP+cell. fibres+ nitrogen	10	23,4	±0,7
	20	23,8	±0,7
	30	22,2	±0,8

Table 8. Impact of cellulose fibres presence and microcellular structure on tensile strength of final composites

The results summarised in tables 7 and 8 showed that with increasing fibre concentration the tensile strength and tensile modulus increased as well. From the initial strength (32,4 ± 0,1 MPa), respectively. modulus (1635 ± 115 MPa) reached by PP matrix the tensile properties were improved up to value of 37.3 ± 0.8 MPa, respectively 2752 ± 82 MPa in the module of elasticity at the highest natural fibres concentrations. When measured the lightweight specimens the tensile strength was reduced up to 22.2 ± 0.8 MPa. In the frame of tensile modulus measurement the reinforcing effect of the fibres was neutralised by the pores and reached values were therefore very similar to the initial values achieved by the PP matrix (max. 1 746 ± 51 MPa), see Fig. 4.
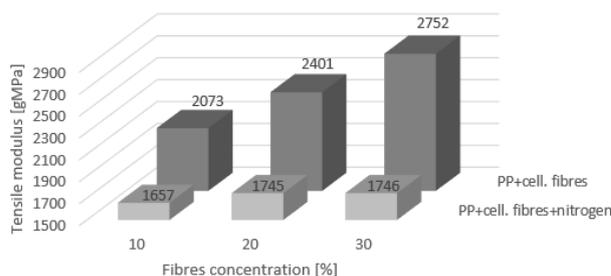
Figure 4. Comparison of reached tensile moduli

5 CONCLUSIONS

The submitted study involves the analyses of the mechanical and physical properties of the polymer composites formed by the polypropylene matrix into which the cellulose fibres were implemented (at the concentrations of 10 wt.%, 20 wt.% and 30 wt.%). The specimens were prepared using conventional injection moulding and using the technology forming the specific microcellular structure using nitrogen as a supercritical fluid.

The density measurement confirmed the higher fibre density compared to the PP matrix leading to linear increase of the density by 4.6% per each 10 wt. % of cellulosic fibres. The density of lightweight systems was reduced by 21% in all analysed systems.

The presence of cellulosic fibres significantly reduced the impact resistance of the composite systems by about 60-67% according to the fillers concentration compared to the values reached by PP matrix. The internal porous microstructure resulted in a further reduction the impact strength of the analysed systems in all cases by approximately 80% of the initial value reached by PP.

The analysis of the flexural properties confirmed the reinforcing effect of the natural fibres. Flexural strength was increased by 20-30% compared to the strength of the PP matrix according to the level of reinforcing. An interesting effect was observed when modifying the structure using SCF (nitrogen). The increase in strength was compensated by the presence of microcellular structure and all the lightweight systems reached values comparable to the initial strength of the PP matrix. Flexural elastic modulus increased linearly with increasing content of the natural fibres in the range from 48 to 77%. The porous structure again reduced the improvement of the flexural moduli those were increased by only 44%, respectively 61% according to reinforcing level.

Tensile properties showed similar trends as the bending ones. The increase in tensile strength induced by the presence of reinforcing fibres was not so significant as in the case of bending strength and maximum measured values rose up by only 15% compared to the values reached by pure PP. In the frame of lightweight specimens analyses the tensile strength obtained approximately only 70% of the initial strength of PP matrix. The significant increase was observed in the tensile modulus of elasticity. Composite systems reached values higher by minimally 26% and maximally 68% compared to the PP depending on the concentration of natural fibres. The porous structure again eliminated the reinforcing effect of the cellulose fibres. Lightweight composites had a modulus of elasticity approximately the same as PP.

Generally, the higher content of natural fibres within the PP matrix foamed by SCF had a stronger impact on the deterioration of the mechanical properties. The reason is probably smaller volume of polymeric matrix which is able to transfer the tension to the reinforcing fibres those are not entirely encapsulated by the matrix.

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