THE DEFORMATION BEHAVIOUR OF HYBRID COMPOSITE SYSTEMS WITH THERMOPLASTIC MATRIXITLE

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Hybrid polymer composites are relatively new group of plastics that are rapidly developed. These materials combine high demands on the mechanical strength while keeping minimal density, thus generally opposing properties. Hybrid polymer composites have potentially very wide applicability, especially in aircraft or automotive industry where weight of the components is one of the critical parameters In the frame of this contribution the effect of individual components of multi-phase systems incorporated into thermoplastic matrix on resulting deformation processes was primarily analyzed. This study includes hybrid composites which are modified for the injection moulding technology. Test specimens for determining the mechanical properties (tensile, bending and Charpy impact) were made of nylon 66 with incorporated fibrous (glass fibres and carbon fibres) and particulate fillers (hollow glass beads / spheres).The final parameterization of individual process steps is very demanding by reason of the composite nature and hybrid structure.

KEYWORDS

reinforced polymers, hybrid composites, mechanical properties, glass fibres , glass spheres, carbon fibres

1 INTRODUCTION

Nowadays the polymer composites belong among widespread and commonly processed plastic materials. Another phases added to the basic polymer matrix primarily modify final mechanical and physical properties of the composite or reduce the final price. With the growing requirements of high-tech applications the demands on such specific products and used materials increase as well. Very often totally contradictory combination of properties must be provided such as high strength of parts with very low weight. Although the plastics have relatively low density comparing to other engineering materials, the emphasis is put on further reduction of their density (or to compensate the effect of high density fillers presence). For these reasons the multi-phase hybrid composite systems were developed that provide effective solutions and meet very high requirements. Flexible modifying the final properties of polymeric materials is allowed by very effective methods of adaptation the interface between polymeric matrix and fillers. These coupling agents or surface treatments increase the frequency of interactions among the individual components of the hybrid composites. All the phases that are included to final multi-component systems have furthermore direct impact on the processing parameters and the shape and dimensional stability of the final part (shrinkage, warpage, dimension accuracy etc.).

2 MATERIALS AND METHODS

In the frame of this study the hybrid composite systems based on the thermoplastic matrix were created and their final properties were modified using the fibrous and particulate filler. The mechanical characteristics were based on standardised analyses (tensile, flexural and impact properties).

The composites are generally defined as heterogeneous systems composed of at least two phases which are significantly different in their physical, mechanical and chemical properties with a sharp phase boundary. The final properties of the composite material are influenced by the properties of individual components, their distribution and mutual interactions. These processes are not exactly predictable and are the result of the synergetic effect. The composites are formed by the continuous phase (matrix) in which the discontinuous phase (reinforcement) is uniformly dispersed. Unlike the alloys (mixing processes based on diffusion principles) the uniform distribution of the discontinuous phase within the composite system must be ensured by mechanical mixing of all components. Broad spectrum of matrixes is currently used (metal matrix composites - MMCs, polymer matrix composites - PMCs, ceramic matrix composites - CMCs, glass matrix composites - GMCs, etc.). From the filler point of view the composite materials may be further categorised according to many criteria (depending on the nature of the filler - reinforcing or non-reinforcing fillers, according to the shape of the filler, according to the size of the filler - nanoscale, microscale, etc.) [Chung 2010, Lipatov 1995, Shalin 1995].

2.1 Polymer composites

Good processibility, corrosion resistance and shock and vibration absorption are particularly the main properties for which the plastic materials are preferred and which are also transferred into composite systems. Transferring tension to the reinforcing filler, the filler protection from environmental impacts and partly from mechanical damage during the processing are dominant roles of the polymer matrix. The matrix should withstand greater deformation than the reinforcement to fully utilize the potential of reinforcing additives. Effective reinforcement is also affected by the orientation of the fibrous filler (considering the orientation of applied forces; when the fibres are oriented perpendicular to the direction of the applied force, the resulting part strength is based primarily on the mechanical properties of the matrix and is minimally affected by the strength of a reinforcing fillers) [Shalin 1995].

The polymer matrix as the continuous phase controls the molecular weight of the composite, phase transmission temperature, morphology structure and the intensity of interactions among the matrix and fillers. With increasing molecular weight of the matrix the viscosity of the polymer melt increases as well and the material reaches better mechanical properties, thermal stability and chemical resistivity. From the applicability point of view the glass transition temperature (Tg) is the most important phase transition temperature. Some fillers may cause shifting Tg to higher temperatures (plasticizer), however, the reinforcing fillers generally increase the glass transition temperature (if they do not increase of water content within the composite material that again acts as an plasticizer). The presence of fillers additionally affects the crystallinity level of the semi-crystalline matrix [Chung 2010, Galasso 1989, Hull 1996].

The resulting effect of the dispersed phase presence depends on the character of the fillers, including the geometry, distribution of shapes and sizes, concentration, the surface profile of the fillers and particularly physical, chemical and mechanical properties. The material must meet high requirements such as thermal stability, chemical resistance, minimal toxicity, good wetting by polymer matrix, compatibility with the polymer and of course the minimum price and good availability to be applicable as a filler [Rosato 2004, Xanthos 2009].

The interfacial area (interphase) is the most important zone from the mechanical properties of the composite point of view because controls the load transfer among the matrix and the fillers. In order to enhance polymer-to-filler interactions, the chemical or physical modification of the particle surface is a widespread used strategy. During the melt-processing, a covalent chemical bond can be formed at the polymer/filler interface by grafting, reactive extrusion or cross-linking techniques. Negative limitation that causes reducing of adhesion among polymer matrix and reinforced fillers is the presence of moisture which could be caused by water molecules interfering in the hydrogen bonding interactions. Coupling agents are employed when two materials are incompatible and these substances with intermediate properties are able to bring the compatibility to the mixture. The coupling agents should enhance very low affinity between non-polar matrix and polar fillers and have two functions: to bond to reactive filler groups and to react with the functional groups of the matrix with the goal of facilitating stress transfer among the fibres and the matrix. The most widely used coupling agents include organosilanes, tryazine and maleic-anhydride. Adding the coupling agents to the matrix changes also the degree of filler dispersion. The chemical modifiers primarily improve the amount of reactive polar groups in the matrix. Non-coupling agents have a great interaction with surfaces of the fillers but they have no chemical bonds with macromolecules of the matrix. Fatty acids are the typical representatives of this modifier type. Coupling modifiers (coupling agent, organosilanes etc.) create on the other hand very strong chemical bonds both with filler surfaces and with the matrix [Sposito 2004, Sterman 1996, Todd 2000].

2.2 Glass fibres

Glass fibres are the most commonly used reinforcing additives for polymer composites (lower price comparing to other reinforcing fillers as carbon fibres or aramid fibres). The category of glass materials involves all inorganic materials that contain more than 50% of silica. From the structural point of view these materials are considered as supercooled liquid (in the glassy state) without any organization of inner structure. The final properties are dependent on the chemical composition and the concentration of basic components (silica, calcium oxide, aluminium oxide and other minerals which are used for the targeted modifying the chemical, physical, mechanical and processing properties). From the health care point of view the inhalation of micro and nano particles is probably the biggest risk. Results of some studies prove that long-term exposure to atmosphere contaminated by the glassy dust can lead to respiratory diseases or even lung cancer. Usual concentration of glass fibres in thermoplastic composites is from 10 to 50 wt. %. For further improvement of polymer composites dimensional stability the mineral fillers (mica, talc etc.) can be added [Rothon 2001, Xanthos 2009].

From the processibility point of view the presence of glass fibres significantly reduces the melt flow of the entire system, which is typically compensated by increasing the pressure (the injection and holding pressure) and temperature (melt temperature and mould temperature). The glass fillers have characteristically high abrasive potential, which must be taken into consideration both in the tool designing process (short and wide inlet channels, coating the running system and the shaped cavities etc.) and in the requirements on machinery equipment (modified injection unit, screw etc.) [Fu 2009].

Glass fibres have typically diameter from 3,5 microns to 20 microns. According to the characteristic properties several types of glasses can be found on the market (since the most common type so-called E-glass to the most expensive and strongest S-glasses).

A-glass (alkaline): the first option for the production of glass fibres are A-glasses which are used for production of bottles and window panels. This glass type is very cheap, however, with low resistance to alkalis.

E-glass (electrical): The glass fibres are preferably produced from specific glass materials that have good elongation and mechanical properties, such as borosilicate glass (E-glass). Marking E implies good electrical insulation properties. High strength, flame resistance and heat resistance during processing, dimensional stability and chemical resistance are another advantages.

C-glass (chemical): High resistance to acids is typical property of C-glasses and that is the reason of using these materials in the chemical industry.

D-glass (dielectric): D-glasses have very low dielectric constant, therefore, they are proffered especially in the electrical, electronics and power applications. The mechanical properties are inferior to E-glasses.

L-glass (low loss): These glasses contain a high proportion of lead and they are characterized by increased impermeability against X-rays. Medical and military applications are typical.

M-glass (modular): Highly modular glass fibres which have higher mechanical rigidity comparing to E-glass fibres, but they are toxic.

S-glass (strength): S-glasses are characterized by higher tensile strength, higher modulus and impact strength comparing to E-glasses. These materials also have higher temperature resistance and were primarily developed for aerospace industry. These fibres have the highest tensile strength of all commonly manufactured glass fibres, even higher than carbon or aramid fibres. The production costs are dramatically higher comparing to conventional E-glasses [Galasso 1989, Hearle 2001].

Comparing to carbon fibres the glass fibres have generally lower modulus, lower fatigue properties and lower resistance at higher temperatures, when the crystallised regions can be distinguish despite the amorphous structural fundamental. Another advantage of glass fibres is the isotropic behaviour.

The absorption of atmospheric humidity may cause the reduce of glass fibre strength by half. The glass fibres are protected by specific surface coating that also improves the wettability of the polymer matrix [Lipatov 1995].

2.3 Carbon fibres

Carbon fibres are characterized by extremely high strength and rigidity, but very low deformability (elongation). Considering the specific strength and modulus of elasticity (per mass unit) the carbon fibres mechanical performances can be excelled by only one applicable reinforcing particle type - single crystal filaments (Al_2O_3 whiskers) [Pritchard 1998].

In the technical literature the term "carbon fibres" involves both the carbon and graphite fibres. The carbon fibres occur at temperatures from 800 ° C to 1600 ° C, whilst graphite fibres are produced at temperatures above 2200 ° C. The carbon content is another criterion of the carbon and graphite fibres differentiation (fibres with carbon content up to 92 wt. % are known as carbon and graphite fibres have higher content of carbon). The carbon fibres are produced by pyrolysis of polyacrylonitrile fibres with typical diameter from 5 µm to 10 µm [5, 20m]. The elastic modulus and the strength of carbon fibres vary within a wide ranges and are dependent primarily on the orientation of individual atoms layers. Therefore, the carbon fibres are characterized by high anisotropy of physical and mechanical properties. The mechanical properties can differ up to 100 times in two different directions of applied force (in the axial direction of the fibre and in the perpendicular direction to the fibre axis). Anisotropy also influences the physical properties such as thermal expansion coefficient etc. [Hearle 2001]. Furthermore, carbon fibres excel by very wide range of mechanical properties, chemical resistivity, low coefficient of friction, thermal stability and favourable fatigue behaviour, excellent electrical conductivity and low density. The polymer composites reinforced with long carbon fibres are particularly suitable for the production of cyclically stressed components primarily for the aviation and military applications. In the frame of machinery engineering, these two-phase systems are used in applications with high requirements on high mechanical properties and low density at the same time [Galasso 1989].

2.4 Hollow glass spheres / beads

Generally, the reinforcing fillers increase the final density of the composites, which can be undesirable effect especially when the weight reducing is one of the main objective of the modification. Using the particulate filler is reasonable solution that have shape of hollow glass spheres or beads, which have only slightly negative impact on the resulting mechanical properties of the part [Rothon 2001]. Glass hollow spheres also improve the processibility of the polymer composite (increasing the flowability, reduced consumption of binding agent, shortening the production cycle etc.) Unlike the other fillers based on minerals such as talc, silica, mica etc. the hollow glass beads have much lower density (glass beads "Q-Cell 'produced by Potters have the density from 0.14 to 0.20 g / cm3). Less weight can reduce transportation costs, enables the production of larger products with improved manipulability. Better dimensional stability, very smooth part surface, improved thermal insulation, better workability and reduced shrinkage are another advantages of the hollow beads usage [Aruniit 2012, Trofimov 2006].

Nowadays, hollow glass beads are widely used in automotive industry. Composites with glass beads can replace the metal components of the driving system, in interior applications or as a part of the bodywork [Xanthos 2009].

2.5 Hybrid composites

In engineering practice the expression "hybrid" is commonly used in conjunction with the "mixing" of different types of materials (often with contradictory tendencies). In the case of polymeric composites the hybridization can be achieved by several ways. The typical approach is combination of two or more types of reinforcing and filling materials added to the matrix or the incorporation of the fillers into the mixture of different matrices (or even the combination of both approaches). Most widespread plastic hybrids are based on mutual combination of fibre reinforcements, such as aramid, carbon and glass fibres [Matthews 1999].

Final properties of hybrid composites are affected by the chemical and structural characteristics, in particular the amount of reinforcing phases (fibres or particulate fillers), orientation and length of fibers, type of reinforcing phase, the distribution of particles and interactions among reinforcing phase and matrix (wettability, adhesion etc.). Successful use of hybrid composites is catalysed by chemical, mechanical and physical stability of the fibre / matrix mixture]. Adding the glass fibres into the composite created by polymer matrix and carbon fibres will induce increasing the impact strength and may considerable reduce the price. Conversely, the adding the carbon fibres into composite reinforced by glass fibre will cause dramatic increasing the flexural modulus [Cambell 2010].

Specific applications of hybrid composites can be found among composites with short glass fibres and carbon fibres (GF / CF) in an epoxy resin, which replaced the steel given for pipes and tanks. These parts have in addition to excellent resistance to creep even good corrosion resistance and sufficient strength. Fatigue strength of hybrids GF / CF / epoxy matrix is utilized in marine applications [Aneli 2014, Rosato 2004].

The hybrid composites may also contain not only synthetic fibres but also the natural fibres considering the impact on the environment. The discontinuous phase can be also incorporated into the biodegradable polymer matrix. (biopolymer hybrids) [Galasso 1989].

2.6 Mechanical properties

The evaluation of mechanical properties of created hybrid composites included several analyzes. Tensile properties test according to ISO 527-2 was one of them and the analysis was carried out using tensile testing machine TIRA 2300 equipped with sensor head 100 kN (10 kN sensing head for evaluation of the modulus of elasticity). Uniaxial tensile load was applied to evaluate the tensile strength (σm), elongation at break (εb) and tensile modulus (Et). Loading rate corresponded to 50 mm / min (1 mm / min for the evaluation of elasticity modulus).

Another analysis was focused on the evaluation of the flexural properties according to ISO 178 carried out with using Hounsfield H10KT with the sensor head size of 500 N and 10 kN. The specimens with rectangular cross-section were loaded by the deformation rate of 2 mm / min. Flexural properties of hybrid composites were characterized by the strength and flexural modulus.

The impact strength was the last analysis involved to this study. The measurement of energy required for breaking defined specimens was performed on testing machine Resil 5.5 CEAST. The analysis followed the ISO 179-1 standard that specifies the Charpy impact test.

3 EXPERIMENT AND RESULTS

Thermoplastic matrix based on nylon 66 (Technyl A218 black 21N) was used for compounding process. Hybrid composites were prepared in laboratories at Technical university of Liberec where nylon 66 was mixed with 7 wt. % of compatibilizing agent Fusabond A560 (to increase cohesion between the matrix and the filler) and with fibrous and particulate fillers. Compounding process and pellets granulation were performed using granulation line ZAMAC EEA - 2x130di. To minimize shear and mechanical damage of the fillers the particles of the discontinuous phase were added into the mixing zone in the front position of the melting chamber. Created material combinations are listed in Tables 1 and 2. To verify the filler content within the hybrid composites the pellets were exposed to the temperature of 850 ° C for 20 minutes according to ISO 3451-4 standard. This heat load decomposed the nylon matrix in a furnace and revealed the fillers content that should be within interval limited by max. 5% deviation.

The shape of multipurpose test specimens followed ISO 3167 and the production process parameters were adjusted in accordance with international standards ISO 294-1 and ISO 1874-2 using injection moulding machine ARBURG 270 S 400-100. The pellets were dried in a vacuum furnace Maguire at the

Table 1. Tensila properties of two phase composite based on nylon 66 with short glass fibres (GF), long glass fibres (LGF) or carbon fibres (CF), σ_m tensile strength, ε_b elongation at break and E_t tensile modulus

Material		σ_m [MPa]	E_t [MPa]	ε_b [%]
PA 66		55,0 ± 0,2	1376 ± 33	> 200 %
PA 66	30% GF	113,7 ± 0,4	6448 ± 97	9,0 ± 0,5
	40% GF	141,6 ± 0,5	9025 ± 162	5,8 ± 0,2
	50% GF	171,3 ± 2,9	12147 ± 261	4,1 ± 0,3
PA 66	30% LGF	134,7 ± 5,1	7504 ± 261	2,9 ± 0,1
	45% LGF	168,9 ± 3,8	11456 ± 331	2,5 ± 0,1
	60% LGF	192,0 ± 5,7	16527 ± 583	1,8 ± 0,1
PA 66	20% CF	141,4 ± 4,3	9590 ± 274	5,4 ± 0,3
	30% CF	175,9 ± 1,6	13929 ± 371	3,7 ± 0,1
	40% CF	215,6 ± 5,8	18853 ± 865	2,8 ± 0,2
PA 66	4% GB	60,7 ± 0,7	1860 ± 46	69,3 ± 8,4
	6% GB	57,1 ± 2,2	1896 ± 44	78,4 ± 11,4
	8% GB	54,6 ± 0,2	1878 ± 22	83,3 ± 15,5
	12% GB	49,9 ± 0,2	1834 ± 26	78,5 ± 6,2

temperature of 80 °C for 4 hours to maximally reduce the water content before injection moulding. Production process was carried out under standard conditions (23 °C and 50% relative humidity). Individual technological parameters were selected considering the standards prescribing the production of nylon test specimens (ISO 1874-2) and the recommendations of material suppliers optimised to eliminate all defects (particularly the sink marks or flashes).

The properties of nylon materials are significantly influenced by the amount of moisture that is bonded in the material structure and that is the reason of conditioning the specimens in the defined atmosphere before carrying out the mechanical tests of the hybrid composites. Conditioning guaranteed the specific moisture content that is equal for all specimens (the equilibrium state of all specimens). To achieve this state the accelerated process of conditioning was employed. The conditioning was carried out at higher temperatures according to ISO 1110 standard and following the ISO 1874-2 standard. The specimens were placed into the climatic test chamber Vötsch VC 0018 preheated to (70 ± 1) ° C and the relative humidity was adjusted to (62 ± 1) %. The conditioning took 10 days. The subsequent testing of mechanical properties was carried out in standard atmosphere (23 ° C and 50% relative humidity). The results are summarized in Tables 1, 2, 3, 4, 5 and 6.

In the first step the tensile properties were analysed (namely tensile strength, modulus and elongation at break). The results revealed the fact that higher amount of hollow glass beads (GB) adversely affects the tensile strength of hybrid composites, however, with respect to density reduction the specific strength is more important property for hybrid composites filled with hollow glass bead. The specific strength is in these cases much higher comparing to the two phase systems fibres / matrix. The strongest effect of hollow glass beads presence on the tensile strength of analysed hybrid composites was observed for materials reinforced with carbon fibre (CF). The values dropped by up to 10%. Hollow glass fibres effected the strength of other hybrid composites as well. In the case of long glass fibres (LGF) reinforced hybrid composites the final decrease of the tensile strength was by about 8%. The weakest impact of hollow glass beads presence was measured during analysis of hybrid composites reinforced with short glass fibres (GF), where higher amount of hollow glass beads did not induce the significant drop of the tensile strength. All hybrid systems reached better mechanical properties than the base matrix and the best results were reached by systems reinforced with carbon fibres. Hybrid composite with 4 GB% and 26.5% CF reached the increase in strength by more than 180% comparing to performance of pure nylon. Very similar results were measured during the analysis of hybrid with 4% GB and 40%LFG. The tensile strength was increased by about 182% comparing to the matrix. On the other hand these mechanical results were induced by higher content of LGF and finally higher density of the hybrid composite (by about 18% comparing to hybrid composite with carbon fibres). The hybrid composite with 4 GB% and 20% carbon fibres reached by about 20% better strength comparing to hybrid composites reinforced with 4 GB% and 20% long glass fibre (LGF) and by about 60% in comparison to the hybrid composites reinforced with 4 GB% and 20% short glass fibres (GF). Finally the density of the hybrid composite with 4 GB% and 20% CF was by about 5% lower than the density of composites with short and long glass fibres. Comparing the effect of short and long glass fibres on the tensile strength better results were reached by hybrid composites containing long glass fibres.

Tensile modulus of elasticity (Et) was another analysed characteristic. The presence of hollow glass beads resulted in increasing the modulus of elasticity in tension of hybrid composites reinforced with carbon and short glass fibers by about 10% comparing to two phase composites. The tensile

Table 2. Tensila properties of hybrid composites based on nylon 66 with short glass fibres (GF), long glass fibres (LGF) or carbon fibres (CF) and hollow glass beads (GB), σ_m tensile strength, ε_b elongation at break and E_t tensile modulus

Material	σ_m [MPa]	E_t [MPa]	ε_b [%]
PA 66 + 4%GB + 13,5%CF	107,3 ± 2,7	7767 ± 86	6,2 ± 0,3
PA 66 + 4%GB + 20%CF	132,9 ± 2,1	10770 ± 239	4,7 ± 0,3
PA 66 + 4%GB + 20%GF	83,5 ± 2,0	4718 ± 41	9,6 ± 0,5
PA 66 + 4%GB + 20%LGF	110,6 ± 5,0	5552 ± 194	3,4 ± 0,2
PA 66 + 4%GB + 26,5%CF	155,9 ± 1,7	13917 ± 168	3,4 ± 0,2
PA 66 + 4%GB + 26,5%GF	103,4 ± 1,5	6322 ± 105	6,8 ± 0,5
PA 66 + 4%GB + 30%LGF	128,4 ± 4,9	7398 ± 140	3,4 ± 0,4
PA 66 + 4%GB + 33,5%GF	122,5 ± 2,1	7859 ± 125	4,7 ± 0,2
PA 66 + 4%GB + 40%LGF	155,0 ± 2,8	9814 ± 210	2,6 ± 0,1
PA 66 + 6%GB + 10%CF	86,1 ± 2,2	5524 ± 170	7,3 ± 0,2
PA 66 + 6%GB + 15%CF	110,2 ± 5,2	8122 ± 237	5,2 ± 0,5
PA 66 + 6%GB + 15%GF	66,4 ± 0,8	3552 ± 120	15,9 ± 1,0
PA 66 + 6%GB + 15%LGF	94,0 ± 2,9	4762 ± 171	3,5 ± 0,1
PA 66 + 6%GB + 20%CF	131,0 ± 5,2	10444 ± 117	4,1 ± 0,6
PA 66 + 6%GB + 20%GF	79,0 ± 3,9	4801 ± 82	9,3 ± 0,5
PA 66 + 6%GB + 22,5%LGF	110,3 ± 1,7	5957 ± 298	3,3 ± 0,0
PA 66 + 6%GB + 25%GF	95,1 ± 1,2	5898 ± 125	5,9 ± 0,6
PA 66 + 6%GB + 30%LGF	130,6 ± 5,1	7411 ± 376	3,0 ± 0,2
PA 66 + 8%GB + 6,5%CF	65,8 ± 1,3	3848 ± 77	9,9 ± 0,8
PA 66 + 8%GB + 10%CF	82,0 ± 0,9	5482 ± 192	7,2 ± 0,5
PA 66 + 8%GB + 10%GF	58,6 ± 0,5	3114 ± 61	17,6 ± 1,3
PA 66 + 8%GB + 10%LGF	71,7 ± 2,7	3534 ± 211	5,7 ± 0,8
PA 66 + 8%GB + 13,5%CF	96,9 ± 2,2	7262 ± 42	5,9 ± 0,3
PA 66 + 8%GB + 13,5%GF	63,1 ± 0,5	3553 ± 78	14,1 ± 0,5
PA 66 + 8%GB + 15%LGF	85,5 ± 2,7	4343 ± 73	3,8 ± 0,2
PA 66 + 8%GB + 16,5%GF	69,0 ± 1,5	3907 ± 71	11,9 ± 0,4
PA 66 + 8%GB + 20%LGF	99,5 ± 5,7	5210 ± 318	3,5 ± 0,2

modulus of hybrid composites reinforced with long glass fibres was not significantly affected by the glass beads. All created

Table 3. Flexural properties of two phase composite based on nylon 66 with short glass fibres (GF), long glass fibres (LGF) or carbon fibres (CF), σ_{fM} flexural strength and E_f tensile modulus

Material		σ_{fM} [MPa]	E_f [MPa]
PA 66		63,0 ± 0,4	1591 ± 61
PA 66	30% GF	198,1 ± 2,3	6804 ± 542
	40% GF	246,0 ± 5,8	9096 ± 549
	50% GF	294,5 ± 2,3	12240 ± 278
PA 66	30% LGF	222,1 ± 8,4	7320 ± 520
	45% LGF	278,8 ± 3,7	11430 ± 540
	60% LGF	351,8 ± 12,9	18315 ± 706
PA 66	20% CF	230,9 ± 2,9	9600 ± 228
	30% CF	279,1 ± 5,4	13860 ± 74
	40% CF	363,8 ± 6,4	21565 ± 561
PA 66	4% GB	69,4 ± 0,3	1884 ± 38
	6% GB	68,9 ± 0,7	1966 ± 60
	8% GB	65,0 ± 0,9	1931 ± 48
	12% GB	64,1 ± 0,3	2018 ± 122

Table 4. Flexular properties of hybrid composites based on nylon 66 with short glass fibres (GF), long glass fibres (LGF) or carbon fibres (CF) and hollow glass beads, σ_{fM} flexural strength and E_f tensile modulus

Material	σ_{fM} [MPa]	E_f [MPa]
PA 66 + 4%GB + 13,5%CF	178,0 ± 3,8	7896 ± 298
PA 66 + 4%GB + 20%CF	219,2 ± 1,9	11088 ± 195
PA 66 + 4%GB + 20%GF	144,3 ± 1,4	4815 ± 372
PA 66 + 4%GB + 20%LGF	185,4 ± 3,9	5952 ± 59
PA 66 + 4%GB + 26,5%CF	254,3 ± 6,3	14490 ± 574
PA 66 + 4%GB + 26,5%GF	184,0 ± 2,1	6744 ± 797
PA 66 + 4%GB + 30%LGF	217,4 ± 4,2	7656 ± 245
PA 66 + 4%GB + 33,5%GF	212,9 ± 4,2	8400 ± 380
PA 66 + 4%GB + 40%LGF	262,9 ± 14,6	10596 ± 717
PA 66 + 6%GB + 10%CF	175,0 ± 7,7	6744 ± 797
PA 66 + 6%GB + 15%CF	174,7 ± 1,6	8208 ± 59
PA 66 + 6%GB + 15%GF	109,3 ± 1,3	3564 ± 150
PA 66 + 6%GB + 15%LGF	157,1 ± 5,6	4728 ± 163
PA 66 + 6%GB + 20%CF	210,3 ± 5,3	10932 ± 450
PA 66 + 6%GB + 20%GF	145,1 ± 7,4	4968 ± 520
PA 66 + 6%GB + 22,5%LGF	186,9 ± 3,5	6120 ± 186
PA 66 + 6%GB + 25%GF	171,1 ± 4,4	6500 ± 358
PA 66 + 6%GB + 30%LGF	213,2 ± 12,3	7848 ± 465
PA 66 + 8%GB + 6,5%CF	95,9 ± 8,0	3716 ± 233
PA 66 + 8%GB + 10%CF	142,1 ± 4,2	6267 ± 189
PA 66 + 8%GB + 10%GF	99,4 ± 1,0	3488 ± 185
PA 66 + 8%GB + 10%LGF	121,6 ± 5,9	3600 ± 280
PA 66 + 8%GB + 13,5%CF	162,4 ± 1,7	7680 ± 228
PA 66 + 8%GB + 13,5%GF	107,9 ± 2,8	3660 ± 204
PA 66 + 8%GB + 15%LGF	152,4 ± 4,0	4671 ± 193
PA 66 + 8%GB + 16,5%GF	118,0 ± 5,0	3951 ± 251
PA 66 + 8%GB + 20%LGF	169,3 ± 2,7	5424 ± 176

hybrid composites reached better tensile modulus comparing to the virgin nylon 66 and the hollow glass beads contributed to reduction of density. The hybrid composite with 4 wt. % GB and 20 wt. % of carbon fibres (CF) reached increasing the tensile modulus by 683% comparing to virgin nylon 66. The hybrid composites reinforced with 20 wt. % short glass fibres (GF) reached the increasing tensile modulus by 243%, and the interaction among long glass fibres (LGF) in concentration of 20 wt. % and hollow glass fibres (4 wt. %) increased the value of tensile modulus by 303% comparing to the matrix. From the tensile modulus point of view the best results were reached by systems reinforced by the carbon fibres. Long glass fibres showed again better mechanical properties than short glass fibres.

Elongation at break (εb) was the last analysed tensile characteristic. The impact of hollow glass beads on the elongation of nylon matrix was significantly negative. The presence of 12 wt. % GB reduced the ductility of pure matrix by about 125%. In the frame of hybrid composites the strongest impact on the elongation was observed in combination of hollow glass beads with carbon fibres or short glass fibres. The interactions among long glass fibres and hollow glass beads did not show significant impact on final elongation at break. The fibrous reinforcement also decreased the ductility of the thermoplastic matrix. The highest values of elongation at break were reached by the composites reinforced with short glass fibres and the lowest values were reached by composites reinforced with LGF. The composites reinforced with carbon fibres showed higher elongation by about 20 ÷ 40 % than hybrid composites reinforced with LGF.

In the next step the flexural characteristics were analysed, i.e. flexural strength (σfM) and flexural modulus (Ef). The presence of hollow glass beads on the flexural strength of hybrid composites has more or less negative effect, however, the fibrous reinforcement improved the ultimate flexural strength of analysed systems. By adding 20 wt. % of carbon fibbers into the nylon matrix the basic flexural strength was increased by 266%. The incorporation of 6 wt. % GB into the composite with 20 wt. % of carbon fibres led to the reduction the final flexural strength by 5% (6 wt. % GB reduced this characteristic by 9%). The dominant benefit of hollow glass beads presence is again the decrease in the overall density of the hybrid composites which results in higher specific strength. Very similar trends were observed during analyses of hybrid composites reinforced with LGF. The hybrid composites containing the short glass fibres did not show any significant changes of flexural strength as the reason hollow glass beads presence. The results again confirmed the strongest impact of carbon fibres on the mechanical properties and more significant influence of long glass fibres than short glass fibres.

Similar to the tensile properties, the presence of hollow glass beads in the hybrid composite systems resulted in increasing in the flexural modulus. Adding 12 wt. % of hollow glass beads into the thermoplastic matrix led to increasing the flexural modulus by 27%. In all cases the incorporation of hollow glass beads into the two phase composites (in the studied interval from 4 wt. % to 8 wt. % GB) had a positive effect on the flexural modulus (increasing from 5 to 15 % comparing to two phase systems). The most significant changes were observed in the frame of hybrid composites reinforced with carbon fibres (CF). The reached values were by up to 86% higher than the flexural modulus of hybrid composites with LGF and by up to 130% higher than the flexural modulus of hybrid composites with short glass fibres (GF).

Table 5. Impact properties of two phase composite based on nylon 66 with short glass fibres (GF), long glass fibres (LGF) or carbon fibres (CF), a_{cU} unnotched impact strength

Material		a_{cU} [kJ/m^2]	type of failure
PA 66		NB	NB
PA 66	30% GF	84,7 ± 4,3	C
	40% GF	84,0 ± 3,6	C
	50% GF	92,5 ± 5,3	C
PA 66	30% LGF	49,6 ± 9,0	C
	45% LGF	70,8 ± 12,7	C
	60% LGF	83,2 ± 11,2	C
PA 66	20% CF	74,2 ± 2,4	C
	30% CF	71,8 ± 5,8	C
	40% CF	84,7 ± 3,2	C
PA 66	4% GB	NB	NB
	6% GB	273,2 ± 13,9	NB
	8% GB	211,0 ± 25,3	NB
	12% GB	112,0 ± 10,1	NB

Charpy impact strength was the last studied parameter (acU). Comparing the two phase composites to hybrid composites the effect of hollow glass beads presence was negative. The particulate fillers reduced the final impact strength. The drop of composite impact strength within the interval from 6 wt. % to 12 wt. % GB was by about 60%. Adding 4 wt. % of hollow glass beads reduced the impact strength of the hybrid composite reinforced with carbon fibres by 27% and 6 wt. % of hollow glass beads reduced the final impact strength of the hybrid composite reinforced with carbon fibres by 33%. Similar trends were reached by hybrid composites with short glass fibres. The results reached by hybrid composites reinforced with LGF revealed the increase in impact strength induced by incorporating of hollow glass beads into the two phase composite (the total increasing the impact strength by up to 34% comparing to two phase composite). The best results among two phase composites were reached by composites reinforced with short glass fibres, however, the worst results were reached by composites reinforced with long glass fibres (LGF). The impact strength was affected by the higher deformability of glass fibres (3 ÷ 5) % comparing to carbon fibres (max. 2%).

4 CONCLUSIONS

The results included in this study implied the range of impacts of hollow glass beads on the final mechanical properties of hybrid composites reinforced with carbon and glass fibres. Higher concentration of hollow glass beads reduced the tensile strength and the density of the composites. On the other hand the positive impact of carbon fibres and long glass fibres presence on the mechanical properties was confirmed. Long glass fibres are more reasonable with respect to the transmission of tensile stresses than short fibres. The rate of alignment of long glass fibres within the composite material is higher than in the case of short glass fibres. Higher stress concentration at the ends of the short glass fibres could be another factor having negative impact on the mechanical properties comparing to systems reinforced with long glass fibres.

Table 6. Impact properties of hybrid composites based on nylon 66 with short glass fibres (GF), long glass fibres (LGF) or carbon fibres (CF) and hollow glass beads,), a_{cU} unnotched impact strength

Material	a_{cU} [kJ/m^2]
PA 66 + 4%GB + 13,5%CF	54,0 ± 4,5
PA 66 + 4%GB + 20%CF	54,4 ± 2,5
PA 66 + 4%GB + 20%GF	58,7 ± 4,6
PA 66 + 4%GB + 20%LGF	57,9 ± 3,2
PA 66 + 4%GB + 26,5%CF	57,7 ± 1,8
PA 66 + 4%GB + 26,6%GF	64,2 ± 3,0
PA 66 + 4%GB + 30%LGF	67,7 ± 3,4
PA 66 + 4%GB + 33,5%GF	68,1 ± 2,3
PA 66 + 4%GB + 40%LGF	73,0 ± 3,3
PA 66 + 6%GB + 10%CF	47,2 ± 5,8
PA 66 + 6%GB + 15%CF	50,7 ± 1,7
PA 66 + 6%GB + 15%GF	68,9 ± 4,8
PA 66 + 6%GB + 15%LGF	53,9 ± 4,4
PA 66 + 6%GB + 20%CF	50,1 ± 3,6
PA 66 + 6%GB + 20%GF	57,4 ± 1,9
PA 66 + 6%GB + 22,5%LGF	62,5 ± 1,9
PA 66 + 6%GB + 25%GF	57,8 ± 3,6
PA 66 + 6%GB + 30%LGF	66,9 ± 2,2
PA 66 + 8%GB + 6,5%CF	64,4 ± 3,2
PA 66 + 8%GB + 10%CF	48,2 ± 3,0
PA 66 + 8%GB + 10%GF	59,9 ± 4,4
PA 66 + 8%GB + 10%LGF	48,9 ± 1,4
PA 66 + 8%GB + 13,5%CF	43,6 ± 2,0
PA 66 + 8%GB + 13,5%GF	57,0 ± 4,6
PA 66 + 8%GB + 15%LGF	53,8 ± 1,4
PA 66 + 8%GB + 16,5%GF	63,0 ± 3,5
PA 66 + 8%GB + 20%LGF	58,8 ± 2,9

The theoretical background implied better deformability of glass fibres comparing to carbon fibres which was confirmed by values of elongation at break. Comparing the results reached by composites reinforced with short and long glass fibres, the long glass fibres demonstrated better mechanical properties which resulted in lower deformability of the composites.

The presence of hollow glass beads in hybrid composites have a combined impact on the flexural behaviour. The flexural strength was reduced with increasing concentration of hollow glass fibres, however, the flexural modulus was increased with increasing concentration of particulate hollow fillers. The fibres have again the positive impact on the flexural behaviour over all studied two phase composites. The best results were reached by composites reinforced with carbon fibres and long glass fibres.

The results from Charpy impact strength analysis confirmed the findings from tensile tests corresponding to elongation at break of hybrid composites. Whilst the composites reinforced with short glass fibres reached the highest values of elongation at break and therefore the highest values of impact strength, the composites reinforced with carbon fibres exhibited lower elongation at break, which therefore corresponded to lower value of the impact strength. On the contrary, in the frame of hybrid composites with long glass fibres the results showed that with higher amounts of fibrous reinforcement the impact strength decreased. This phenomena may be again connected to specific alignment of long glass fibres. Generally, the incorporation of hollow glass fibres into the nylon matrix or composites reinforced with fibrous fillers reduced the deformability of the polymer composites.

As the conclusion of this study the fact should be emphasized that the presented results implied only trends of mechanical behaviour of hybrid composites based on combination of fibrous and particulate fillers in the thermoplastic matrix. However, the final properties in real applications are significantly influenced by many factors (material, technological parameters, part design etc.). The performances are dependent on the distribution of fibres in the polymer matrix, interaction and adhesion of the fibres to the matrix, moisture content and other aspects that may affect the results. Injection moulding is very specific technology, especially for processing of material with heat sensitive additives or brittle fillers, which are strongly affected by the technological parameters.

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