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Development of Basalt Fiber Reinforced Injection Molded Polyamide Composites

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1. Introduction

Thermoplastic matrix composites have gained great importance in the last 30 years. The most common processing technology of thermoplastic matrix composites is injection molding, which is capable of producing products in large quantities with good dimensional accuracy and complex geometry. In the last two decades basalt fibers have come into consideration as potential reinforcement of composite materials.

Basalt fibers possess several good properties which make it possible to use them as a reinforcement in composites. They are incombustible and chemically inert. Also, basalt fibers are environmentally and ecologically harmless, and free of carcinogens and other health hazards. Basalt fibers have been comprehensively investigated as reinforcement of polypropylene matrix composites. Polyamide has been seldom used for this purpose, although it promises better results, because polyamide and basalt both have polar chemical structure, thus presumably it is easier to promote proper interface adhesion between the fibers and the matrix. It must be also noted that polyamides have better mechanical properties and higher heat resistance than polypropylene. The glass fiber reinforced polyamide is a vital engineering material in automotive and other industries today. Most car manufacturers employ glass fiber reinforced polyamide intake manifolds and sumps in their engines.

One of the most significant problems of injection molded composites is the formation of proper interfacial adhesion between the matrix and the fibers. It is particularly relevant because during processing the strong shearing stresses reduce the length of glass fibers to the order of magnitude of a few tenths millimeters, regardless of their original size. Thus the critical fiber length must be decreased by promoting the interfacial adhesion. In case of basalt fiber reinforced polyamide composites the technology of surface treatment must be developed in order to get composite materials which are comparable with glass fiber reinforced ones. The experiences gained with glass fibers can be used as basis due to the virtually same structure and similar chemical composition of basalt and glass fibers.

2. Analysis of literature

The main goal of reinforcing thermoplastics with fibers – besides enhancing mechanical properties – is the increasing of heat deflection temperature, stiffness, creep resistance, wear resistance and toughness, altering of electric properties or decreasing the thermal expansion coefficient. Thermoplastic matrix composites are mainly reinforced with glass, carbon, ceramic and natural fibers. The different properties of thermoplastic matrix

composites are strongly influenced by the residual length of fibers. Fibers fragment during compounding and plastification in the injection molding machine. During injection further fragmentation occurs in the nozzle and the mold, meanwhile the average length decreases generally to 0.2 to 0.4 mm. This length is often under the critical fiber length, hence short fiber reinforcement is unable to utilize the full possibilities of fiber reinforcement. The most appropriate fiber length is between 3 and 6 mm. According to literature data increasing the fiber length to this range may increase the tensile strength of composites with 120%, but further increasing of the fiber length does not cause considerable additional growth in strength. The attainable fiber length depends on the geometry of the product and the injection molding speed. For example in a product with 1.5 mm wall thickness the attainable average fiber length is approximately 30% smaller than in a product with 4 mm wall thickness. The manufacturing technologies of long fiber reinforced thermoplastics can be divided into two groups: they are compounded on in-line blending units directly before processing (direct processing, D-LFT) or supplied as ready-to-use pellets (P-LFT). P-LFT compounds – which can be processed by conventional injection molding machines – can be made by a variety of manufacturing processes, the principal difference between them being whether the fibers are cable coated (here specially treated glass fibers are enclosed within a plastic coat and not impregnated until processed) or fully impregnated (here the fibers are impregnated with the plastic matrix, in the compounding process). The roving impregnated or coated with the matrix is cut into pieces with a length between 10 and 55 mm. If special cautious injection molding parameters are employed, the fragmentation of fibers can be decreased, thus fiber length can be largely retained. Special screws and the preheating of pellet helps to further decrease fiber fragmentation. D-LFT technologies employ complex machine lines which incorporate compounding and molding in one unit. These methods enable the manufacturing of parts with large dimensions and up to 100 mm residual fiber length.

3. Materials and methods

Types and markings of used reinforcing materials are shown in Table 1. Matrix materials are shown in Table 2.

Marking	Type of fiber	Manufacturer
SB	Short basalt fiber	Toplan (Hungary)
CB1	Continuous basalt fiber	Kamenny Vek (Russia)
CB2	Continuous basalt fiber	D.S.E. Group (Israel)
CB3	Continuous basalt fiber	Technobasalt (Ukraine)
GF	E-glass fiber	Johns Manville (Slovakia)

Table 1. Types and markings of used reinforcing materials

Type	Name	Manufacturer
PA6	Schulamid 6MV13F	A. Schulman GmbH (Germany)
PA6.6	Akulon S223-E	DSM N.V. (Holland)
PA6	Factor PA6	FACT GmbH (Germany)

Table 2. Types and markings of used matrix materials

The mechanical properties of the fibers were investigated by tensile tests. The elementary fibers were stuck to paper windows and their diameter was measured on a Projectina 4014/BK-2 projection microscope fitted to an image processing system and equipped with a CCD camera, with 400× magnification. The diameter of fibers was measured at three different points to determine the variations in diameter. Subsequently the specimens were clamped to the testing machine, the paper window was cut and the fiber was tensioned. The tests were executed according to the EN ISO 5079:1999 standard, with 25 mm gauge length on a Zwick Z002 testing machine, at ambient temperature. The test speed was v=2 mm/min. 100 specimens of each material were tested and the mean values and standard deviations were calculated. The chemical composition of the fibers was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) method, using a Labtest Plasmalab ICP spectrometer. The amount of oxides was calculated from the elementary composition. Silane and titanate coupling agents are applied on the surface of fibers during fiber manufacturing. In the industry coupling agents are only one of many components of sizings. The functions of sizing are protection of fibers, assuring processability and enhancing interfacial adhesion. In our experiments the original sizing of basalt fibers – applied by the manufacturer – was removed and a new coupling agent was applied, by

immersing the fiber in the solution of coupling agent and subsequent drying. This enables the formation of a coating of coupling agent, although we must lack those components of the sizing which have other functions. The currently available continuous basalt fibers are covered with sizings optimized for epoxy, vynilester and polyester resins. The methods of enhancing interfacial properties of PP-basalt composites are worked out, while it is still necessary to find the appropriate technology for polyamide matrix composites. The coupling agents developed for glass fiber reinforced composites are applicable for basalt fibers, due to the similarities between the structure and chemical composition of basalt and glass fibers.

All materials were dried for 5 hours at 80ºC before processing. The specimens were made with an Arburg 270 C 500-250 injection molding machine.

The specimens were subjected to different static and dynamic mechanical tests. Three point bending tests were carried out according to the ISO 178 standard. The span length was 64 mm, the test speed was 2 mm/min. Tensile tests were carried out according to the ISO 527 standard. Gauge length was 100 mm, the test speed was 2 mm/min. Elongation was measured with video extensometer. Prior to mechanical tests the specimens were conditioned on 20°C and 50% relative humidity.

Charpy impact test were conducted on a CEAST Resil Impactor instrument according to the EN ISO 179 standard with notched and unnotched specimens. The notches were *A* type with 2 mm depth, 0.25 mm fillet radius and 45° angle. The energy of the hammer was 15 J and the impact speed was 3.3 m/s. The specimens were 80 mm long with 62 mm span length and 4×10 mm cross section. The falling weight tests were performed using 80×80×2 mm plate specimens with a Ceast Fractovis 6785 instrument. The mass of the falling weight was 23.62 kg. The spear of the falling weight ends in a hemispherical head with 20 mm diameter. The tests were executed with 150 J impact energy and 3.56 m/s impact speed. The injection molding shrinkage of materials was investigated with the plate specimens also used for falling weight tests. The instructions of EN ISO 294 standard were taken as a basis for shrinkage measurements. Dynamic Mechanical Analysis (DMA) tests were performed with specimens machined from the injection molded tensile specimens. Tests were executed with dual cantilever configuration and force control on a Perkin-Elmer Diamond DMA instrument. The cross section of specimens was 2×4 mm, the frequency was 1 Hz. Parameters of DMA tests are shown in Table 3.

Parameter	Value
Specimen width, z [mm]	4
Specimen thickness, y [mm]	2
Span length, x [mm]	30
Force amplitude, F_0 [mN]	400
Heating speed [°C/min]	2
Temperature range [°C]	-40…180

Table 3. Parameters of DMA tests

The residual fiber length in the injection molded specimens was determined in the following way: pieces cut from the middle section of dumbbell specimens were calcinated in ceramic pots with gas flame and in electric oven at 500°C. The fibers were spread on glass slides using formic acid as carrier fluid. The length of fibers was measured with an Olympus BX51 optical microscope and analySIS Steel Factory image analysis program, employing through lighting and magnification of 10. The length of 500 fibers was measured from each sample.

The surfaces of basalt fibers with different coatings were examined with Fourier transform infrared spectroscopy (FTIR). Tests were performed with a Varian Scimitar 2000 instrument. Here the sample is pressed between a diamond and a sapphire. The sample is illuminated through the diamond with infrared light in the wavenumber range between 400 and 4000 cm^{-1}. The reflected light arrives to the spectrometer through the same diamond. The applied samples were the bunches of 6 mm long chopped basalt fibers. This method is capable of detecting the presence of coupling agents on the surface of basalt fibers through identifying atom groups of the silane compounds. Quantitative examination is restrictedly possible by this technique.

Fiber orientation in injection molded specimens was measured the following way: the central part of dumbbell specimens was cut and polished 2D sections were made in the middle longitudinal plane of the specimens by an Olympus BX51 optical microscope and AnalySIS Steel Factory image analysis software. The specimens were divided into 10 sections (each 0.4 mm wide) and micrographs were made of the sections. The fibers appear as elliptical figures on these micrographs. The length of the major and minor axis of the ellipse was measured. The orientation angle was calculated from the major and minor axis of the ellipse.

4. Theses

1. It was proven that basalt fibers made by continuous technology are appropriate for reinforcing PA6 and PA6.6 matrix composites. Compounded and injection molded composites with 10, 20, 30 and 40 wt% basalt fiber reinforcement have outstanding mechanical properties, with 40 wt% reinforcement the tensile strength can be raised to 300% compared to the tensile strength of the matrix. Basalt fibers permit of the production of injection molded products with mechanical properties comparable to glass fiber reinforced composites.

2. It was investigated, that strong linear relationship exists between the tensile strength and joint SiO_2+Al_2O_3 content of basalt fibers made by continuous and Junkers technology in the range between 60 and 70 wt%. The gradient and the constant term of the $\sigma=a\cdot C-b$ equation possess the following values in the applied experimental system: a=128 MPa/m%, b=7000 MPa, where σ [MPa] is the average tensile strength of fibers and C [m%] is the joint SiO_2 and Al_2O_3 content of basalt fibers.

3. On the basis of dynamic mechanical analysis of PA6 and PA6.6 matrix composites reinforced with basalt fibers sized with different coupling agents in the -40…170°C temperature range, it was proven that the comparison of loss factor and storage modulus are suitable for the qualification of fiber-matrix interface. It was investigated, that the peak height of loss factor curve is in coherence with the quality of fiber-matrix interface in the temperatures of glass transition and above that. Lower loss factor peak height and higher storage modulus refer to stronger adhesion.

4. It was investigated, that the average residual fiber length in PA6 and PA6.6 matrix composites made by compounding and injection molding with uniform technology parameters, reinforced with basalt fibers with different sizings, can be characterized by the $l_f=-A\cdot c+B$ equation as the function of fiber content in the 10-40 wt% range. In the equation c [m%] is the fiber content, l_f [mm] is the average residual fiber length, B [mm] and A [mm/m%] are constant terms. In case of investigated composites the B constant is between 0.16 and 0.30 depending on the type of matrix and sizing, while the value of A constant is 0.0020±0.0004 mm/m%.

5. Solution surface treatment was applied for producing basalt fiber reinforced PA6 matrix composites. The best results were provided by the coupling agent 3-glycidoxypropyltrimethoxysilane (applied in a 4 wt% ratio of basalt fibers). In case of 30 wt% basalt fiber reinforced composites the tensile strength grew with 42%, the flexural strength grew with 37% and the impact strength grew with 223% compared with unsized composite. The presence of coupling agents on the surface of basalt fibers was proven by Fourier transform infrared spectroscopy.

6. It was proven by comparing basalt fiber reinforced injection molded PA6 matrix composites made by long fiber thermoplastic technology and conventional compounding, that:
   a: The application of cautious injection molding parameters and long fiber thermoplastic technology enables the formation of composites with an average fiber length/diameter ratio of 130, in spite of conventional compounded short fiber reinforced composites where the fiber length/diameter ratio is 14. The perforation energy and Charpy impact strength of long fiber reinforced composite is more than 100% higher than that of the short fiber reinforced composite. Dynamic mechanical analysis revealed that the application of long basalt fibers increases the storage modulus with 10% and decreases the loss factor with the same extent compared to short fiber reinforced composite.
   b: The fiber orientation in long basalt fiber reinforced products fundamentally differs from short basalt fiber reinforced ones. This results in more isotropic molding shrinkage in case of long basalt fiber reinforced composite, its warpage factor is 30% smaller than that of the short fiber reinforced composite.

5. List of publications

Hungarian conference lectures

1. **Deák T**., Czigány T.: A szálgyártási technológia hatása a bazaltszálak mechanikai és geometriai tulajdonságaira, Anyagvizsgálat a Gyakorlatban Konferencia, Tengelic (2006)
2. **Deák T**., Czigány T.: Bazaltszállal erősített poliamid mátrixú kompozitok vizsgálata, VI. Országos Anyagtudományi Konferencia, Siófok (2007)

English conference lectures

3. **Deák T**., Kovács J. G.: Study of mechanical properties of injection molded basalt fiber reinforced polyamide composites, 23rd Danubia-Adria Symposium, Slovakia, Podbanské, (2006)
4. **Deák T**., Czigány T.: Development of basalt fiber reinforced polymer composites with thermoplastic matrix, Materiais 2007 Conference, Portugal, Porto (2007)
5. **Deák T**., Czigány T.: Investigation of mechanical properties and chemical composition of basalt fibers, 3rd China-Europe Symposium on Processing and Properties of Reinforced Polymers, Budapest (2007)

Hungarian journal articles

6. **Deák T**., Kovács J. G., Szabó J. S.: Bazaltszál-erősítésű fröccsöntött poliamid zsugorodásának vizsgálata, Műanyag és Gumi, 41 (2004), 443-451.
7. **Deák T**.: A fröccsöntési zsugorodás és a technológia összefüggése, Műanyagipari Szemle, 2(2) (2005), 23-29.
8. **Deák T**., Kovács J. G., Szabó J. S.: Bazaltszál-erősítésű fröccsöntött poliamid mechanikai tulajdonságainak vizsgálata, Anyagvizsgálók Lapja, 15 (2005), 88-92.
9. **Deák T**.: Bazaltszál – az üvegszál vetélytársa, Műanyagipari Szemle, 5(3) (2008), 23-28.
10. Czigány T., **Deák T**.: Folytonos bazaltszállal erősített poliamid mátrixú polimer kompozit szerkezeti anyag fejlesztése, Műanyag és Gumi, 47 (2010), 63-68.

English conference articles

11. **Deák T**., Kovács J. G.: Investigation of the molding shrinkage of basalt fiber reinforced injection molded polymer composites, Fifth Conference on Mechanical Engineering, Budapest, CD proceeding, p. 6 (2006)
12. **Deák T**., Czigány T.: Effect of fiber surface treatment on mechanical properties of basalt fiber reinforced thermoplastic matrix polymer composites, Sixth Conference on Mechanical Engineering, Budapest, CD proceeding, p. 7 (2008)

13. Czigány T., **Deák T**., Tamás P.: Investigation of mineral fiber reinforced polypropylene matrix composites, 13th European Conference on Composite Materials. Stockholm, CD proceeding, p. 9 (2008)
14. **Deák T**., Czigány T., Balogh G., Maršálková M., Kovačič V., Militký J.: Thermomechanical properties of basalt fiber reinforced polyamide composites. Proceedings of 15th International Conference 'STRUTEX' on Structure and Structural Mechanics of Textiles. Liberec, Czech Republic, (2008), 33-40.
15. **Deák T**., Czigány T.: Temperature dependent behavior of mineral fiber reinforced composites, Eighth Conference on Mechanical Engineering, Budapest, CD proceeding, p. 8 (2010), *submitted: 2010*

English journal articles

16. Vas L. M., Pölöskei K., Felhős D., **Deák T**., Czigány T.: Theoretical and experimental study of the effect of fiber heads on the mechanical properties of non-continuous basalt fiber reinforced composites, Express Polymer Letters, 1 (2007), 109-121.
17. **Deák T**., Czigány T.: Investigation of basalt fiber reinforced polyamide composites, Materials Science Forum, 589 (2008), 7-12.
18. **Deák T**., Czigány T., Tamás P., Németh Cs.: Enhancement of interfacial properties of basalt fiber reinforced nylon 6 matrix composites with silane coupling agents, Express Polymer Letters, *submitted: 2010.*
19. Czigány T., **Deák T**., Tamás P.: Discontinuous basalt and glass fiber reinforced PP composites from textile prefabricates: Effects of interfacial modification on the mechanical performance, Composite Interfaces, 15 (2008), 697-707. *IF=0,690*
20. **Deák T**., Czigány T.: Chemical composition and mechanical properties of basalt and glass fibers: A comparison, Textile Research Journal, 79 (2009), 645-651. *IF=0,779*
21. **Deák T**., Czigány T., Maršálková M., Militký J.: Manufacturing and testing of long basalt fiber reinforced thermoplastic matrix composites, Polymer Engineering and Science, *accepted, 2010, IF=1,245*