

EFFECT OF THE FILLER SHAPE ON THE PROPERTIES OF RIGID POLYURETHANE FOAM AT CRYOGENIC TEMPERATURE

V. Yakushin*, U. Cabulis, I. Sevastyanova

Latvian State Institute of Wood Chemistry, Dzerbenes 27, LV-1006, Riga

*yakushin@edi.lv

Keywords: polyurethane foam, carbon fibers, glass microspheres, cryogenic temperature.

Abstract

The effect of the filler shape and volume content on the properties of low-density rigid polyurethane foams at cryogenic temperature was investigated. Mechanical properties of foams filled with milled carbon fibers with an average length of 100 and 60 μm and glass microspheres with an average diameter of 65 μm at 77 K were compared. A considerable increase of modulus of elasticity in compression in the foam rise direction with increasing filler content was observed. Compressive strength of foams in both directions at cryogenic temperature upon the loading of milled carbon fibers of both types decreased. Compressive strength of foams with a density of 90 kg/m^3 somewhat increased only upon the loading of glass microspheres.

1. Introduction

To improve the mechanical properties of foams, various types of fillers are used, differing, first of all, by the geometrical sizes and shape [1]. The smallest of them are nanoparticles, the sizes of which are much less than the sizes of the foams' cellular structure elements [2,3]. On the other pole are chopped fibers, the length of which, estimated in mm, is much greater than not only the sizes of the cellular structure elements, but also the foam cells themselves [4,5]. Naturally, the mechanism of reinforcement of those foams is its own in each case [6]. The intermediate location between those two groups of fillers is filled by milled fibers and disperse particles of different shape [7,8]. Their sizes, estimated in μm , are comparable with the sizes of the foams' cellular structure elements.

The effect of the reinforcement of foams upon the loading with such fillers depends, first of all, on the quality of dispersing the particles of the filler in the foam's volume, as well as on the density of the foam itself. The quality of dispersing the filler depends, to a great extent, on the filler's concentration in the polymeric matrix. The optimal content of the filler for each type of the filler, depending on its shape, may be different.

In the previous works, on the example of two types of milled carbon fibers of different length and on the example of glass hollow microspheres, the effect of the filler shape and volume content on the properties of low-density rigid polyurethane foams at room temperature has been investigated [9-11]. In the present study, the effect of the mentioned factors on the mechanical properties of filled foams at cryogenic temperature (77 K) is evaluated.

2. Materials and testing methods

Milled carbon fibers Tenax®-A HT M100 of two types with an average length of 100 (50-150) and 60 (40-70) μm and a diameter of 7 μm , as well as hollow glass microspheres of 3M Scotchlite™ type K1 with an average diameter of 65 (15-125) μm were used as fillers. All the fillers were preliminarily loaded in a polyol mixture, representing a composition of polyethers and polyesters of the Elastogran Group with the total OH value 597 mg KOH/g, as well as catalysts and a surfactant.

After the careful stirring and deaeration, the necessary amount of the blowing agent Solkane 365/227 (87:13) was added to the composition, and mixed again. Then the corresponding amount of the polyisocyanate Voratec SD 100 of Dow Chemical was added and mixed with the help of a laboratory mixer at a stirrer rotational speed of 2000 rpm during 10-12 s. The mixed polyurethane composition was poured into open 250×250 mm molds.

The amount of the blowing agent was varied to obtain series of polyurethane foam blocks of filled and neat foams of different density (from 55 to 90 kg/m^3). The amount of the loaded filler was also varied. In the present study, the maximal content of the filler, which enabled the quality mixing of the filled compositions and obtaining of foam blocks with a minimal quantity of defects, for milled carbon fibers was 12 wt.%, and for glass microspheres – 5 wt.% of the total amount of polyurethane foam, except for the amount of the blowing agent. Taking into account the density of carbon fibers 1780 kg/m^3 and true density of glass microspheres 125 kg/m^3 , the maximal volume content of the filler in the foam for milled carbon fibers and glass microspheres was equal to 8.4 and 34 %, respectively.

Owing to the used process methods and certain corrections, described in detail in [10], series of blocks of polyurethane foams with minimum variations in their thickness (50-60 mm) were obtained, while the density of polyurethane foams in each series only insignificantly differed from the assigned values (55, 65, 80 and 90 kg/m^3).

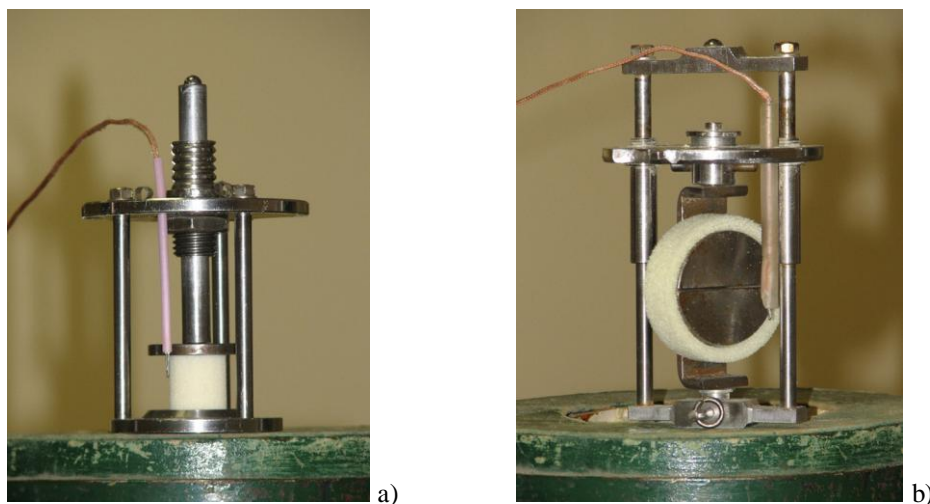


Figure 1. Appliances for foam samples compression (a) and tension (b) at cryogenic temperatures.

A Static Materials Testing Machine Z100 (Zwick GmbH & Co. KG) with 1 kN force cell and the basic program testXpert V11.02, a compact cryogenic facility (cryostat) and special appliances for compression and tension of the original construction, described in detail in [12], were used for foam samples testing at 77 K. Cylindrical samples, 20 mm in diameter and

22 mm in height, were used for compression testing (Fig. 1, a). The foam's compressive properties were determined in parallel (z) and perpendicular (x) directions to the foam rise. Ring samples, 13-14 mm in width, with the inner diameter 43 mm and the outer diameter 53 mm (Fig. 1, b), were used for tensile characteristics determination. The strain rate in all tests was 10%/min.

3. Results and discussion

The technology used for filled polyurethane foams' preparation allowed obtaining foam blocks with a homogeneous structure and a uniform distribution of the filler in the foam volume. In particular, coefficient of variation for most of the determined properties was in a range of 5-10%. Certain defects were found only in the cross-sections of the polyurethane foam blocks with high filler content. Those were small air bubbles, caught during polyurethane components' stirring and not floated at the surface of the very viscose polyurethane composition before the onset of the foam rising process.

Since the density of polyurethane foams in different series of blocks of the filled foams, despite the technological corrections, somewhat differed from one another, approximating relations between the characteristics of the filled polyurethane foams and their density were obtained for each content of the filler. Similar approximating dependences were also found for the neat polyurethane foam.

The properties of the filled polyurethane foams were compared with those of the neat polyurethane foam of a specified density. When the actual density of a foam somewhat differed from the given one, for comparison, the values of the characteristics, corrected according to the corresponding approximating relation, were taken. It should be noted that, as in the case of room temperature [11,12], the relations between the characteristics of the polyurethane foams at cryogenic temperature in compression and their density (in the range of the investigated densities), with a high accuracy, were approximated by linear dependences, while those in tension – by polynomial dependences of the second degree. In most cases, the coefficient of determination R^2 was within a range of 0.95-0.98.

The results of the above comparison are presented further in Figures in relative units (ratios between the values of the characteristics of filled and neat foams). An analysis of these results revealed the following tendencies.

With increasing volume content of the fillers, moduli of elasticity in compression for the foams at cryogenic temperature varied approximately as at ambient temperature. Thus, modulus of elasticity in compression in the foam rise direction (E_z) for the foam with a density of 90 kg/m³ increased to the greatest extent upon the loading of 100 μ m long milled carbon fibers (CF 100). At the maximal content (8.4%) of these fibers, modulus of elasticity increased by 30% (Fig. 2). The increase of modulus of elasticity in the foam rise direction for the foams filled with 60 μ m long milled carbon fibers (CF 60) was much lower. Modulus of elasticity upon the loading of 15% glass microspheres (GM K1) increased by 20%. In this case, for the foams filled with glass microspheres, at the same content of microspheres, modulus of elasticity in perpendicular direction to the foam rise (E_x) also increased by the same 20%. For the foams filled with milled carbon fibers, the increase of modulus of elasticity in compression in perpendicular direction was slightly lower.

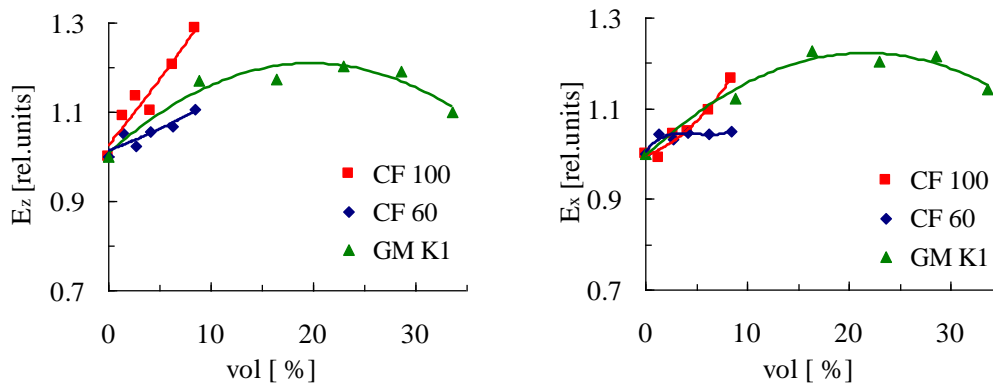


Figure 2. Moduli of elasticity in compression in parallel E_z and perpendicular E_x directions for 90 kg/m³ foam vs. filler content.

Somewhat different effects were observed for the foams of lower density (55 kg/m³) (Fig. 3). Modulus of elasticity in compression in the foam rise direction increased to a greater extent upon the loading of 8.4% of 60 μ m long milled carbon fibers (by 30%). In the case of loading the foam with 100 μ m long milled carbon fibers, modulus of elasticity in the foam rise direction increased by 15% at the volume content of fibers 4.2%. At the further increase in the content of these fibers, modulus of elasticity in compression in the foam rise direction decreased. For the foam filled with glass microspheres, with increasing content of the filler, modulus of elasticity in the foam rise direction increased only by 15%.

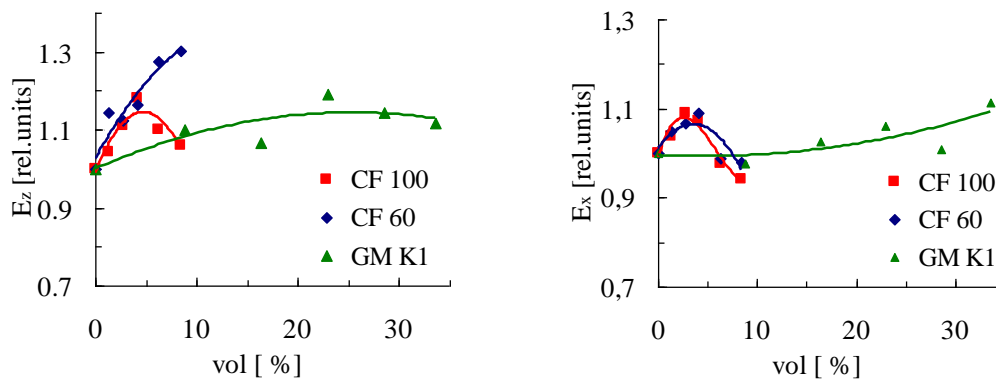


Figure 3. Moduli of elasticity in compression in parallel E_z and perpendicular E_x directions for 55 kg/m³ foam vs. filler content.

The increase of modulus of elasticity in compression in perpendicular direction to the foam rise for the foams with a density of 55 kg/m³ upon the loading of glass microspheres was negligible. Upon the loading of 4.2% milled carbon fibers, modulus of elasticity of the foams increased by 10%. At a greater content of milled carbon fibers, modulus of elasticity in perpendicular direction of the foams decreased.

A similar character of the variation in moduli of elasticity in compression for filled foams is explained, as shown in the previous studies [11,12], by the corresponding distribution and orientation of the fillers in the cellular polymeric framework. In foams of greater density, at a small content, the filler was sufficiently well dispersed in the polymer in the form of separate fibers and microspheres. The fibers were located mainly in the cell struts oriented in the foam

rise direction. In the foams of the lowest density, a considerable amount of fibers was located in the perpendicular direction to the foam rise. Microspheres, in contrast to fibers, were located mainly in cell nodes. At a higher content, quality dispersing of the filler in the polymeric matrix was not possible, and besides separate fibers or microspheres, numerous small bundles of fibers or microsphere agglomerates were observed in the cellular framework. Those agglomerates disturb the homogeneity of the cell structure and are actually the main defects that worsen the mechanical properties of filled foams.

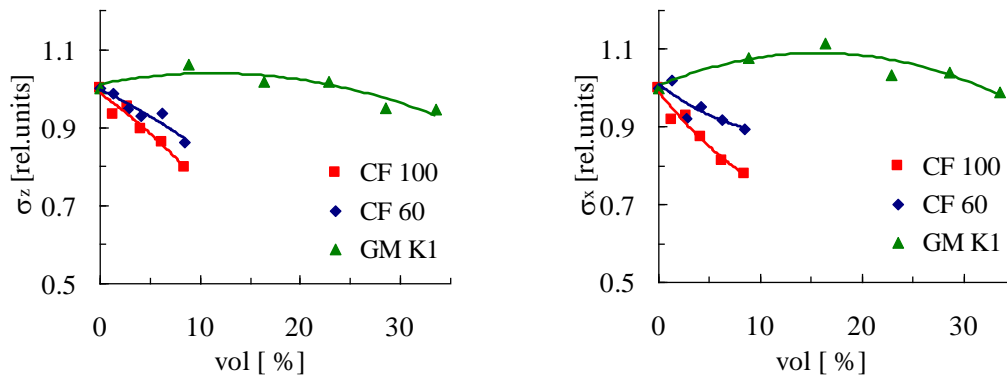


Figure 4. Compressive strength in parallel σ_z and perpendicular σ_x directions for 90 kg/m³ foam vs. filler content.

Compressive strength of the foams at cryogenic temperature varied quite in a different manner than in the case of ambient temperature. Thus, at increasing content of glass microspheres, the compressive strength of the foam with a density of 90 kg/m³ in both parallel (σ_z) and perpendicular (σ_x) direction to the foam rise increased by no more than 5% (Fig. 4). Still at the increasing content of milled carbon fibers, the foam's strength at cryogenic temperature in both directions notably decreased. In this case, it decreased to a greater extent upon the loading of 100 μ m long milled carbon fibers. For the foams with a density of 55 kg/m³, the pattern was even worse (Fig. 5). The drop in strength upon the loading of milled carbon fibers was even greater. In this case, compressive strength for foams in perpendicular direction to the foam rise was much greater than that in the foam rise direction. Also the strength of the foams filled with glass microspheres decreased in this direction.

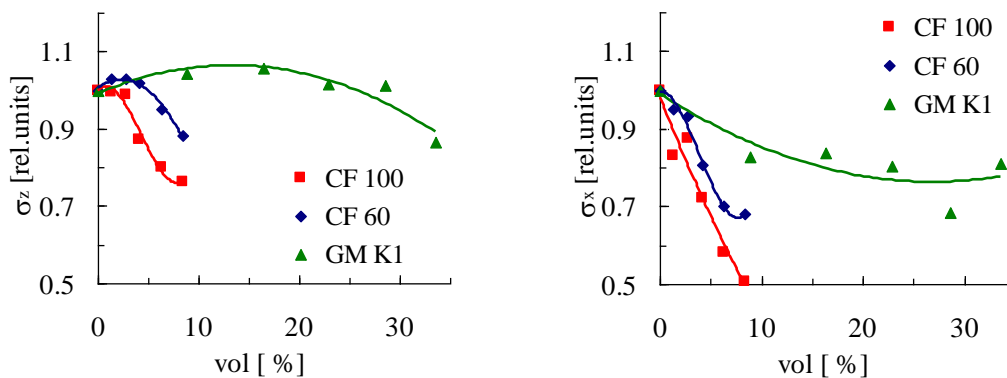


Figure 5. Compressive strength in parallel σ_z and perpendicular σ_x directions for 55 kg/m³ foam vs. filler content.

The obvious reason for the drop in strength at cryogenic temperatures upon the loading of fillers is the difference in the coefficients of thermal expansion of the filler and the polymer. In this case, when using carbon fibers, this difference is very great. Owing to the difference in coefficients of thermal expansion at the deep cooling, thermal stresses take place in the cell structure of the filled foam, causing non-negligible initial damages, which decrease the strength of the foam. Similar effects at cryogenic temperatures were observed also by other researchers [13].

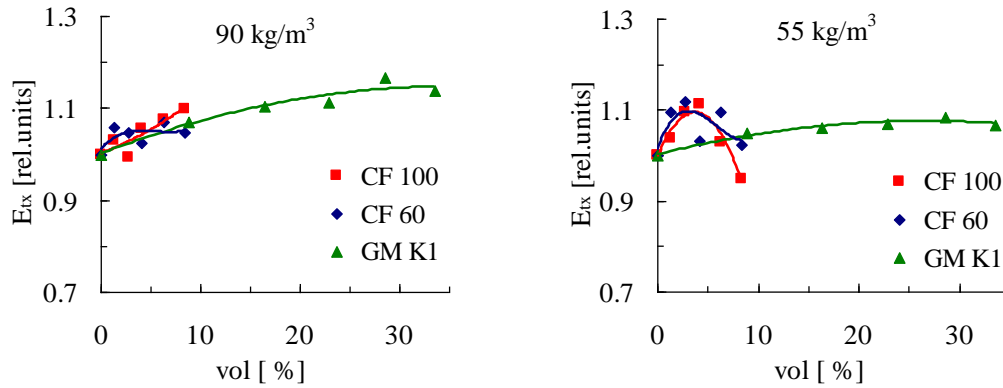


Figure 6. Modulus of elasticity in tension in perpendicular direction for 90 and 55 kg/m³ foams vs. filler content.

Upon the loading of all mentioned fillers, modulus of elasticity in tension in perpendicular direction to the foam rise (E_{tx}) at cryogenic temperature increased approximately as the modulus of elasticity in compression. For the foams with a density of 90 kg/m³ at increasing content of each of the mentioned fillers, the modulus gradually increased (Fig. 6). For the foams with a density of 55 kg/m³ only in the case of loading glass microspheres at increasing content of the filler, modulus of elasticity also gradually increased. For the foams filled with milled carbon fibers, modulus of elasticity increased only at increasing content of the filler up to 4.2%. At the further increase in the content of milled fibers, modulus of elasticity in perpendicular direction decreased.

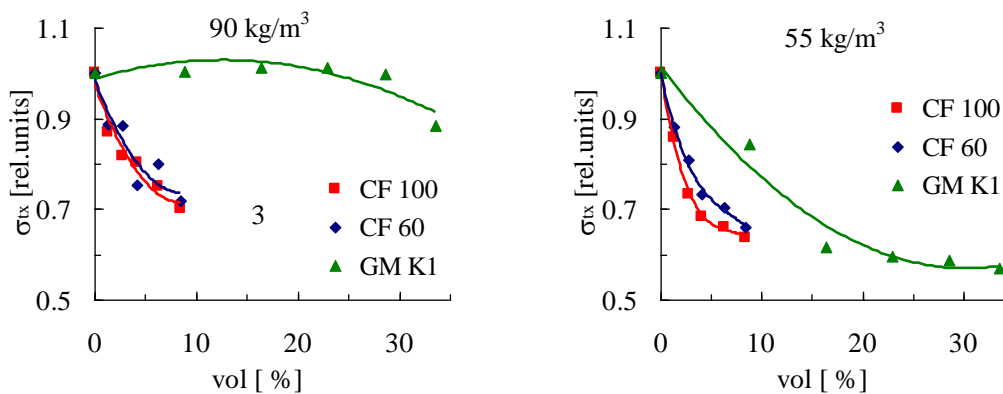


Figure 7. Tensile strength in perpendicular direction for 90 and 55 kg/m³ foams vs. filler content.

Tensile strength in perpendicular direction (σ_{tx}) at cryogenic temperature only upon the loading of glass microspheres negligibly increased for the foams with a density of 90 kg/m³. For the foams with a density of 55 kg/m³, at increasing content of glass microspheres, tensile strength at cryogenic temperature decreased (Fig. 7). Upon the loading of milled carbon

fibers, the strength of the foams of all the densities decreased. In this case, the decrease in strength was the greater the less was the density of the foam and the longer the fibers.

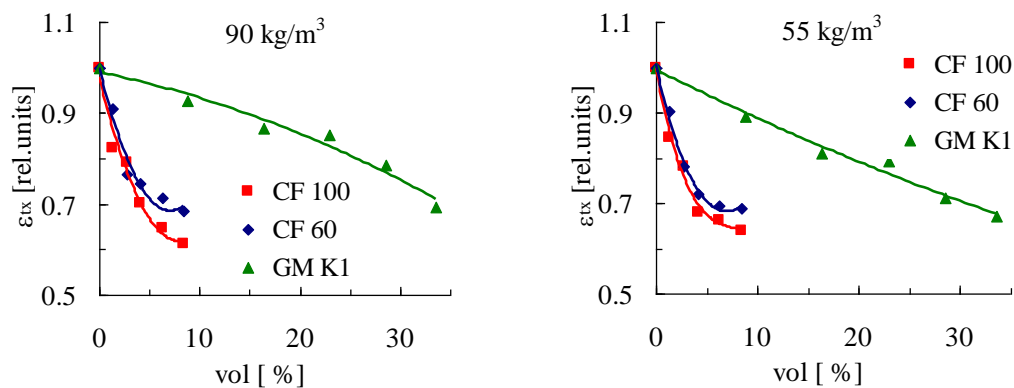


Figure 8. Elongation at break in perpendicular direction for 90 and 55 kg/m³ foams vs. filler content.

Elongation at break (ϵ_{xx}) at cryogenic temperature upon the loading of all the mentioned types of fillers decreased (Fig. 8). This occurred to a lesser extent in the case of loading glass microspheres. Elongation at break decreased to a greater extent upon the loading of 100 μm long milled carbon fibers. At such a notable drop of tensile elongation, the decrease in density of the foam turned to be much lower than in the case of the compressive strength in perpendicular direction to the foam rise.

4. Conclusions

Upon the loading of fillers, moduli of elasticity of the foams at cryogenic temperature tend to increase. In this case, modulus of elasticity in the foam rise direction for the foams filled with milled carbon fibers increase to the greatest extent.

Compressive and tensile strength of the foams with a density of 90 kg/m³ at cryogenic temperature upon the loading of glass microspheres remains approximately on the same level. Upon the loading of milled carbon fibers, both compressive and tensile strength at cryogenic temperature for the foams decrease.

Acknowledgement

The present study is a result of the many years' co-operation with ASTRIUM GmbH.

References

- [1] O. G. Tarakanov, I. V. Shamov, V. D. Alperin. *Filled Plastic Foams*. Khimiya, Moscow, 1988 (in Russian).
- [2] V. Dolomanova, J. C. M. Rauhe, L. R. Jensen, R. Pyrz and A. B. Timmons. Mechanical properties and morphology of nano-reinforced rigid PU foam. *Journal of Cellular Plastics*, 47(1):81-93, 2011.

- [3] L. Chen, R. Ozisik, L. S. Schadler. The influence of carbon nanotube aspect ratio on the foam morphology of MWNT/PMMA nanocomposite foams. *Polymer*, 51(11):2368-2375, 2010
- [4] A. Siegmann, S. Kenig, D. Alperstein and M. Narkis. Mechanical behavior of reinforced polyurethane foams. *Polymer Composites*, 4(2):113-119, 2004.
- [5] M. Kuranska, A. Prociak. Porous polyurethane composites with natural fibres. *Composites Science and Technology*, 72(2):299-304, 2012.
- [6] J. M. Methven, J. R. Dawson. Reinforced Foams. In Hilyard N. C., editor, *Mechanics of Cellular Plastics*, pages 323-358, Scientific and Technical Books, New York, 1982.
- [7] I. W. Schamow, W. P. Tscherepanov, O. G. Tarakanow, J. A. Petrow. Anwendung zerkleinerter Glasfasen als modifizierender Zusatz für Polyurethanhartschaumstoffe. *Plaste und Kautschuk*, 26(1):23-25, 1979.
- [8] J. A. Hagarman, J. P. Cunnion and B. W. Sands. Formulation and physical properties of polyurethane foam incorporating hollow microspheres. *Journal of Cellular Plastics*, 21(6):406-408, 1985.
- [9] V. Yakushin, U. Stirna, L. Belkova, L. Deme and I. Sevastyanova. Properties of rigid polyurethane foams filled with milled carbon fibers. *Mechanics of Composite Materials*, 46(6):679-688, 2011.
- [10] V. Yakushin, L. Belkova and I. Sevastyanova. Properties of rigid polyurethane foams filled with glass microspheres. *Mechanics of Composite Materials*, 48(5):579-586, 2012.
- [11] V. Yakushin, L. Belkova, I. Sevastyanova. Effect of the filler shape on the properties of rigid polyurethane foam. In: *Proceedings of the 15th European Conference on Composite Materials*, Venice, Italy, 8 pages, 2012.
- [12] V. A. Yakushin, N. P. Zhmud' and U. K. Stirna. Physicomechanical characteristics of spray-on rigid polyurethane foams at normal and low temperatures. *Mechanics of Composite Materials*, 38(3):273-280, 2002.
- [13] A.-G. Denay, S. Castagnet, A. Roy, G. Alise and N. Thenard. Compression behavior of glass-fiber-reinforced and pure polyurethane foams at negative temperatures down to cryogenic ones. *Journal of Cellular Plastics*, 49(3):209-222, 2013.