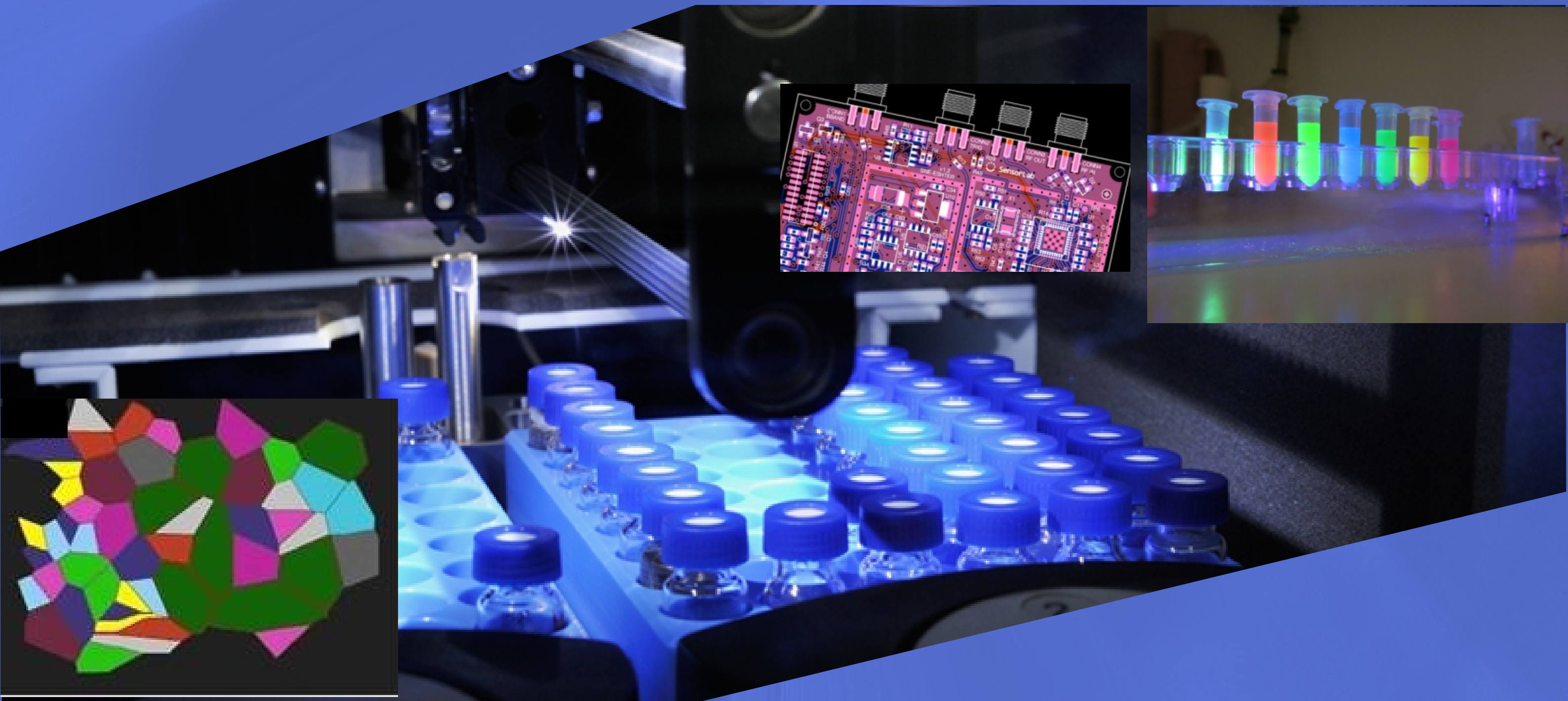
MEDNARODNA
PODIPLOMSKA ŠOLA
JOŽEFA STEFANA

8. ŠTUDENTSKA KONFERENCA MEDNARODNE PODIPLOMSKE ŠOLE JOŽEFA STEFANA

Zbornik - 1. del

8th JOŽEF STEFAN INTERNATIONAL POSTGRADUATE SCHOOL STUDENTS' CONFERENCE

Proceedings - Part 1



31.5 - 1.6. 2016, Ljubljana

Zbornik 8. Študentske konference Mednarodne podiplomske šole Jožefa Stefana
(Proceedings of the 8th Jožef Stefan International Postgraduate School Students' Conference)

Uredniki / Editors:
Majda Pavlin
Janja Vidmar
Ana Kroflič
Johanna Amalia Robinson
Klemen Bregar
Aleksander Matavž

Založnik / Publisher:
Mednarodna podiplomska šola Jožefa Stefana, Ljubljana

Dosegljivo na / Attainable at:
http://ipssc.mps.si/2016/Proceedings8_IPSSC_2016_Part1.pdf

Ljubljana, maj 2016

Konferenco organizira Študentski Svet Mednarodne podiplomske šole Jožefa Štefana
(The Conference is organized by Jožef Stefan International Postgraduate School - IPS Student Council)

CIP - Katabožni zapis o publikaciji
Narodna in univerzitetna knjižnica, Ljubljana

5/6(082)(0.034.2)
378.046-021.68:001.891(497.4)(082)(0.034.2)

MEDNARODNA podiplomska šola Jožefa Stefana. Študentska konferenca (8 ; 2016 ; Ljubljana)
Zbornik [Elektronski vir]: 1. del = Proceedings part 1/ 8. študentska konferenca Mednarodne podiplomske šole Jožefa Stefana = 8th Jožef Stefan International Postgraduate School Students' Conference, 31. maj in 1. junij 2016, Ljubljana, Slovenija ; [organizira študentski svet Mednarodne podiplomske šole Jožefa Stefana = organized by Jožef Stefan International Postgraduate School - IPS Student Council] ; uredili, edited by Majda Pavlin ... [et al.]. - El. knjiga. - Ljubljana : Mednarodna podiplomska šola Jožefa Stefana, 2016

Način dostopa (URL): http://ipssc.mps.si/2016/Proceedings8_IPSSC_2016_Part1.pdf

ISBN 978-961-94034-0-2 (pdf)
1. Pavlin, Majda, 1988- 2. Mednarodna podiplomska šola Jožefa Stefana (Ljubljana)
284835328

8. ŠTUDENTSKA KONFERENCA MEDNARODNE PODIPLOMSKE ŠOLE JOŽEFA STEFANA

Zbornik – 1. del

8th JOŽEF STEFAN INTERNATIONAL POSTGRADUATE SCHOOL STUDENTS' CONFERENCE

Proceedings – part 1

Uredili / Edited by

Majda Pavlin, Janja Vidmar, Ana Kroflič, Johanna Amalia Robinson, Klemen Bregar in Aleksander Matavž

31. maj in 1. junij 2016, Ljubljana, Slovenija

Organizacijski odbor / Organising Committee

Majda Pavlin
Janja Vidmar
Ana Kroflič
Johanna Amalia Robinson
Klemen Bregar
Maja Somrak
Aleksander Matavž
Andraž Bradeško
Barbara Breznik

Redakcijski odbor / Technical Review Committee

prof. dr. Ester Heath
prof. dr. Nives Ogrinc
prof. dr. Janez Ščančar
doc. dr. Zdenka Šlejkovec
prof. dr. Janja Vaupotič
prof. dr. Borut Smodiš
doc. dr. Gašper Tavčar
prof. dr. Stojan Stavber
doc. dr. Miha Čekada
prof. dr. Spomenka Kobe
doc. dr. Boštjan Jančar
doc. dr. Maja Ponikvar-Svet
prof. dr. Aleš Švigelj
doc. dr. Tomaž Javornik
prof. dr. Marko Bohanec
doc. dr. Leon Žlajpah
doc. dr. Damir Vrančič
prof. dr. Bogdan Filipič
prof. dr. Marko Debeljak
prof. dr. Nada Lavrač

Končna komisija za oceno prispevkov in predstavitev / Final commission for the evaluation of contributions and presentations

prof. dr. Radmila Milačič (predsednik komisije / commission head)
prof. dr. Milena Horvat (ECO professor)
prof. dr. Boris Žemva (ECO/NANO professor)
prof. dr. Barbara Malič (NANO professor)
doc. dr. Tomaž Klobučar (ICT professor)
Majda Pavlin (predstavnica študentov / student representative)

Kazalo (Table of Contents)

Microstructural analysis of Bulk Molding Compounds and correlation with the flexural strength

Barbara Bertoncelj[1,2,], **Katarina Vojisavljević**[3], **Janez Rihtaršič**[1], **Gregor Trefalt**[4], **Barbara Malič**[3]
[1] Domel, d.o.o., Železniki, Slovenia
[2] Jožef Stefan International Postgraduate School, Ljubljana, Slovenia
[3] Department of Electronic ceramics, Jožef Stefan Institute, Ljubljana, Slovenia
[4] University of Geneva, Sciences II,Quai Ernest-Ansermet 30, 1205 Geneva, Switzerland
barbara.bertoncelj@domel.com

Abstract. In this study, the influence of the glass fiber (GF) content on the microstructure and flexural strength of bulk molding compounds (BMCs) is investigated. Three sets of BMCs with different weight fractions of GF (5/10/12.5 wt%) were commercially prepared and compression molded into test specimens. The microstructure of the composites was analysed by scanning electron microscopy and further quantitatively characterized by Voronoi analysis in order to define the degree of the fiber distribution homogeneity. The experimental results were compared to the modelled microstructures. The results revealed that the fiber distribution in the composite with 5 wt% of GF is considered as the most homogeneous. Through the obtained microstructural descriptors, the fiber weight content and their distribution were correlated to the flexural strength of BMCs. The flexural strength was the highest for the composite with 10 wt% of GF.

Keywords: bulk molding compounds, glass fibers, microstructure, Voronoi analysis, flexural strength

1 Introduction

Bulk molding compounds (BMCs) are composite materials, consisting of a polymer matrix, discontinuous glass fibers (GF) and a mineral filler. Generally, polymers have low strength and stiffness, therefore the addition of GF improves the mechanical strength of the material. BMCs are highly filled with the mineral filer, which modifies the viscosity of the polymer resin, improves the dimensional stability and surface quality, gives self-extinguishing properties and lowers the cost of the material. Finally, the function of the polymer is to hold together the fibers and particles of the filler in a proper spatial arrangement and helps in the stress transfer between the glass fibers. The overall properties of BMC composites are influenced by the weight content of individual constituents and their properties as well as on the type, shape, orientation and distribution of fibers.

The main area of application of such materials is in the electro and electronic industry for manufacturing of various products, ranging from switches and connection boxes to components for assembly of electro motors, such as housings, brush holders and yokes. The second major utilization area of such materials is automotive industry, e.g. for manufacturing under-the-hood components and headlamp reflectors. BMC products are usually manufactured by the injection molding technology, mainly used for mass production of small, complex shaped components.

The orientation and spatial distribution of fibers in the material depends on the molding process as well as on the geometry of the mold that is used to manufacture the composite product. Therefore, the formed product exhibits a complex microstructure with the preferred orientation of GF in the filling flow direction. However, the inhomogeneous fiber distribution can lead to a poorer mechanical strength of the material [1,2].

The Voronoi diagram analysis is one of the methods that can be used to quantitatively describe the microstructure of the fiber reinforced composites. In this way the microstructure can be described with statistical parameters in order to identify the level of the fiber distribution homogeneity. Several authors have applied Voronoi method to describe the microstructure and distribution of the second phases in composite materials [3-7]. The same method was used in our previous work, where we investigated the fiber distribution homogeneity in BMC composites with different GF fractions and where we concluded that the fiber distribution inhomogeneity affects the mechanical response of the composites. More details can be found in [8].

In this work we investigated another set of BMC samples with different weight contents of GF (5/10/12.5). Thus, the Voronoi diagram method was used to identify and quantify the level of the fiber distribution homogeneity. Furthermore, the results of Voronoi analysis were related with the flexural strength of composites.

2 Experimental work

Three sets of BMC composites with varying contents of GF and mineral filler were commercially prepared. The polymer phase, based on the thermosetting unsaturated polyester, styrene and additives, was kept constant (21 wt%), while the GF with the initial length of 4.5 mm and diameter of 11 μm (confirmed by the scanning electron microscopy, SEM) were used for the polymer reinforcement. $CaCO_3$ was used as the mineral filler [9]. The formulation of the samples is listed in Table 1. Test specimens were prepared by compression molding, according to the standard ISO 3167 [10].

Table 1: Composition of the BMC samples.

	Polymer matrix	GF	$CaCO_3$
	Content [wt%]		
1	21	5	74
2	21	10	69
3	21	12.5	66.5

For individual composition, the test specimen was cut in half, perpendicular to the filling flow direction of the compound during the molding in order to obtain cross sections for microstructural characterization, as shown in Figure 1. The cross-sections of the test specimens were prepared by the standard metallographic technique, i.e. by grinding and polishing, and examined by field-emission scanning electron microscope FE-SEM (JSM-7600F JEOL Ltd., Tokyo, Japan). Prior to the SEM observations the samples were sputter-coated with a thin carbon layer. The micrographs were taken at the accelerating voltage of 15 kV in backscattered-electron mode.

The Voronoi diagrams were generated from the SEM micrographs. First, the center of each glass fiber on the micrograph was marked with a black point using Corel Paint Shop Pro X7 software. Next, the Voronoi diagrams were constructed using ImageJ software and then the area of each Voronoi polygon was measured using Image Tool software. Nine SEM micrographs of an individual sample were included in the analysis (see Figure 1) which accounts for 1.6 mm^2 of investigated area for each sample. As a reference, for each composition of the composite material, a pattern of randomly distributed disks (by Poisson process) and a corresponding Voronoi diagram were generated.

For an easier comparison of the samples with different fractions of fibers, the absolute areas were normalized to the relative polygon areas, A_r, according to Equation (1):

$$A_r = A_p N / A_{total} \tag{1}$$

where A_p is the absolute polygon area, N is the number of polygons in the sample, A_{total} is the area of the sample. For individual sample, histograms of relative Voronoi polygon areas were generated.

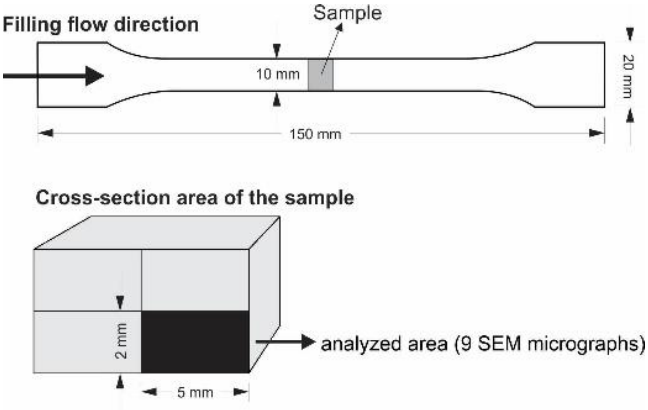


Figure 1: Schematic representation of the test specimen's dimensions, the cutting position of the sample and the sampling scheme of the cross-sectional area for the morphological characterization.

The flexural strength of the test specimens was measured by the three-point bending method (Alpha 50-5), according to standard ISO 178:2003 [11]. The span between the supports was 64 mm and the crosshead speed was 2.0 mm/min. The test was carried out on 15 specimens of each composition and calculated by the equation (2),

$$\sigma_f = \frac{3Pl}{2bh^2} \tag{2}$$

where σ_f is the flexural strength, P is the maximum fracture load, l is the span between the supports, b is the width of the sample and h is the height of the sample.

3 Results and discussion

3.1 Microstructure and Voronoi analysis

SEM micrographs of cross-sectional areas of the BMC composites with corresponding experimental and random Voronoi diagrams are shown in Figure 2. During the molding process, the fibers tend to orient in the preferred direction, i.e. they are mostly oriented parallel with the filling flow of the material. Therefore, depending on the orientation of the fibers, the cross-sections of the GF are circular to elliptical. The fibers are surrounded by the irregularly shaped particles of the $CaCO_3$ mineral filler. From the micrographs we observed that at lower glass fiber content, i.e. at 5 wt% to 10 wt% of GF, the distribution of the fibers is quite homogeneous. However, by increasing the glass fiber content above 12.5 wt%, the fibers tend to cluster together, forming a non-homogeneous microstructure with local areas where the number of fibers (i.e. fiber clusters) is high and areas filled only with polymer resin and $CaCO_3$ mineral filler.

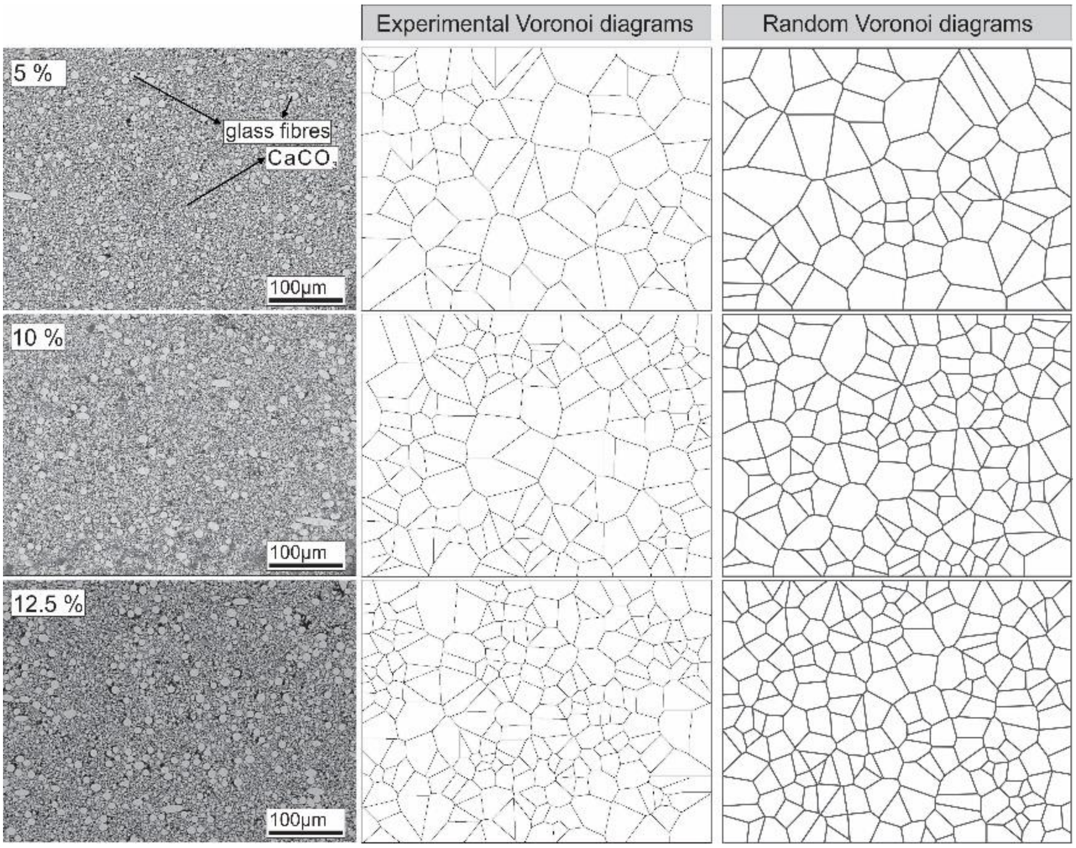


Figure 2: SEM micrographs of the BMC composites with different weight fractions of GF (5, 10 and 12.5 wt%) and the corresponding Voronoi diagrams from the experimental and randomly generated fiber distribution.

Therefore, in the next step we quantitatively characterized the microstructures to evaluate the homogeneity of the fiber distribution in the polymer matrix. To distinguish between the microstructures with possible fiber clustering and a more even fiber distribution in the polymer matrix, the experimental Voronoi diagrams were compared with Voronoi diagrams from the randomly generated microstructures (see Figure 2, central and right column). The experimental Voronoi polygons for the sample with 5 wt% of GF are quite large, but when the fiber content increases the polygons become smaller as a consequence of a larger number of fibers and therefore smaller spatial distances between them. Furthermore, it can be seen that there are more obvious differences between the sizes of polygons in experimental Voronoi diagrams of the samples with 10 and 12.5 wt% of GF. This is especially pronounced in the latter sample where relatively small polygons indicate fiber clustering. On the other hand, the sizes of Voronoi polygons obtained from random microstructures are almost equal across the whole area - as a result of a homogeneous fiber distribution.
The histograms of relative Voronoi polygon areas from the experimental and random fiber distributions are shown in Figure 3. For the sample with 5 wt% of GF the experimental and random distribution plots are very close to each other, which confirms an even and homogeneous fiber distribution. However, we would like to note, that from the viewpoint of mechanical performance such composition could not be treated as the best since the mechanical properties are dependent on the fiber distribution as well as on fiber content (see section 3.2 Flexural strength).

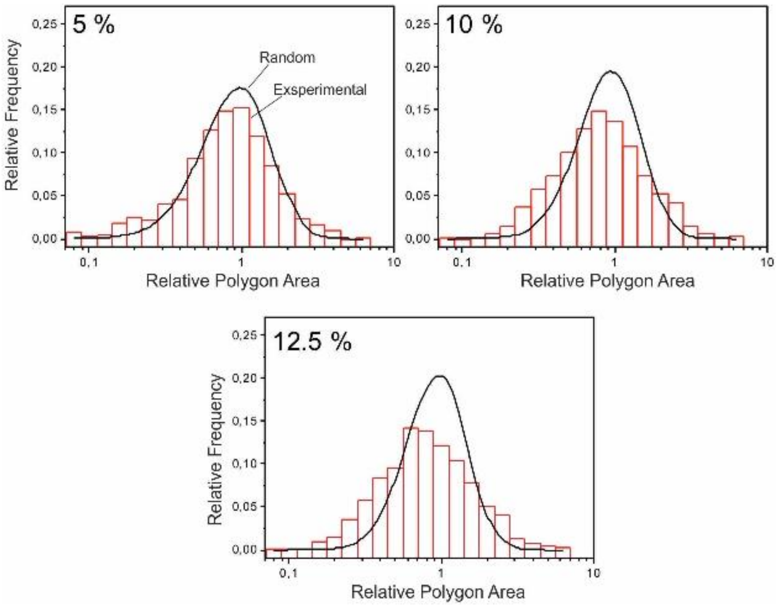


Figure 3: Histograms of the relative Voronoi polygon areas of BMC composites for the experimental and randomly generated fiber-distribution microstructure.

With increasing the GF content, the divergence of the experimental plot from the random plot is more pronounced, especially in the sample with 12.5 wt%. This indicates fiber clustering in the microstructure as a consequence of shorter distances between the fibers, i.e. only on local areas and not on the whole pattern.

The distribution of the random Voronoi polygons is becoming narrower with increasing the GF content which implies a more even distribution at higher fiber fractions. On contrary, the experimental distributions of all BMC samples have a similar width, with a peak slowly shifting to lower values when the GF content increases, which suggests that the fiber clustering is more prominent in the samples with ahigher fiber content due to the lack of space for a homogeneous fiber distribution.

3.2 Flexural strength

The results of the flexural strength measurement and standard deviation of the BMC composites with different weight fractions of GF are listed in Table 2. The flexural strength is increasing with GF content from 61 MPa for the sample with 5 wt%, reaching a maximum value of 82 MPa for the sample with 10 wt% of GF. However, with further increase in the fiber content the flexural strength decreases to 76 MPa, which could be related to increased contacts between the fibers that contribute to the less efficient stress transfer in the composite material. The value of standard deviation for the latter sample is the highest (±7) indicating uneven load capacity. Even so, that the decrease in flexural strength from 82 to 76 MPa is within the experimental error, the deterioration of flexural strength and uneven load capacity can be a consequence of fiber clustering that is reflected in non-homogeneous fiber distribution. This is more pronounced in the composites with higher fiber contents, i.e. in the sample with 12.5 wt% of GF as confirmed by Voronoi analysis, cf. Figures 2, 3.

Table 2: Flexural strength and standard deviation of BMC composite samples.

	GF content [wt%]		
	5	10	12.5
σ_f [MPa]	61 ± 3	82 ± 5	76 ± 7

4 Conclusions

Voronoi diagram analysis was used to quantitatively characterize the microstructures of BMCs with different weight fractions of GF and to correlate the derived microstructural features with the flexural strength of the composites. According to the results of Voronoi analysis the fiber distribution in the sample with 5 wt% of GF most closely approximates to the values of the random distribution. With increasing the fiber content, the divergence from the random distribution is more pronounced, especially in the sample with 12.5 wt%, which indicates fiber clustering at higher fiber contents. Such non-homogeneity of the fiber distribution can then affect the mechanical performance of the composites. The flexural strength increases with increased fiber content, however, only to a certain level. The highest value was measured for the sample with 10 wt%. A suitable combination of properties, i.e. a high level of fiber distribution homogeneity and high flexural strength can be achieved by tailoring the glass fiber content in BMCs. Moreover, the microstructure in critical parts of complex shaped BMC products from serial production can be quantitatively analyzed with Voronoi diagrams to obtain information about the fiber distribution. In this way the microstructure can be related to the mechanical response of the material which may be useful if mechanical testing cannot be performed, for example due to a non-standard shape of a selected part.

Acknowledgements

B.B. gratefully acknowledges the financial support of the Ministry for education, science and sport of Republic of Slovenia and European Commission through the European Social Fund. B.M. and K.V. acknowledge the support of the Slovenian Research Agency (P2-0105).

References:

[1] L. T. Harper, T. A. Turner, N. A. Warrior, J. S. Dahl, C. D. Rudd. Characterisation of random carbon fibre composites from a directed fibre preforming process: Analysis of microstructural parameters. *Composites Part A: Applied Science and manufacturing*, 37: 2136-2147, 2006.

[2] V. S. Sreenivasan, D. Ravindran, V. Manikandan, R. Narayanasamy. Mechanical properties of randomly oriented short Sansevieria cylindrica fibre/polyester composites. *Materials and Design*, 32: 2444-2455, 2011.

[3] M. J. G. W. Heijman, N. E. Benes, J. E. ten Elshof, H. Verweij. Quantitative analysis of the microstructural homogeneity of zirconia-toughened alumina composites. *Materials Research Bulletin*, 37:141-149, 2002.

[4] G. Trefalt, A. Benčan, M. Kamplet, B. Malič, Y. Seo, K. G. Webber. Evaluation of the homogeneity in Pb(Zr,Ti)O3–zirconia composites prepared by the hetero-agglomeration of precursors using the Voronoi-diagram approach. *Journal of the European Ceramic Society*, 34:669-675, 2014.

[5] J. Summerscales, F. J. Guild, N. R. L. Pearce, P. M. Russell. Voronoi cells, fractal dimensions and fibre composites. *Journal of Microscopy*, 201:153-162, 2001.

[6] Z. Sun, X. Zhao, J. Ma. Characterization of microstructures in sisal fiber composites by Voronoi diagram. *Journal of Reinforced Plastics & Composites*, 32:16-22, 2012.

[7] Z. Samardžija, U. Kunaver, M. Čeh, S. Novak. Determination of ZrO_2 distribution in an Al_2O_3 matrix by digital image analysis and point pattern analysis. *Scanning* (17):186-191, 1995.

[8] B. Bertoncelj, K. Vojisavljević, J. Rihtaršič, G. Trefalt, M. Huskić, E. Žagar, B. Malič. A Voronoi-diagram analysis of the microstructures in bulk-molding compounds and its correlation with the mechanical properties. *Express polymer letters* 10 (6): 493-505, 2016.

[9] B. Bertoncelj, K. Vojisavljević, J. Rihtaršič, G. Jelenc, B. Malič. Characterization of glass fiber reinforced composites for housing of electrical motors. In A. Žemva (Ed.), P. Šorli (Ed.), I. Šorli, (Ed.). *Proceedings of the 49th MIDEM International Conference on Microelectronics, Devices and Materials*, Kranjska Gora, Slovenia, 2013.

[10] ISO 3167: Plastics-Multipurpose test specimens. International Organization for Standardization. https://www.iso.org.

[11] ISO 178:2003: Plastics. Determination of flexural properties. International Organization for Standardization. https://www.iso.org.

For wider interest

Bulk Molding Compounds (BMCs) are a combination of polymer matrix, glass fibers and $CaCO_3$ mineral filler. Each constituent is having its own role that contributes to the final properties. The latter are dependent on chemical and physical properties of individual constituents, their relative amounts and spatial orientation and distribution of fibers.

BMCs are a preferred replacement for metals, such as steel and aluminum, because of their properties such as high strength and stiffness in combination with low density, low thermal expansion, corrosion resistance, etc. Moreover, the manufacturing process (injection molding) is energy efficient. Because the product is made in one piece there is no need for additional operations, such as machining and drilling.

The main use of BMCs is in mass production of components and products in automotive, electro and electronic industry. In such products, the mechanical response, for example, flexural strength, is important, but is sometimes hard to measure due to the complexity of the shape. Therefore, the microstructural analysis, i.e. Voronoi diagram analysis, can be applied to critical parts of BMCs products to obtain an insight about the mechanical response and to identify the causes for products failure or poor quality.