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Morphological aspect of multilaminar PP composite

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ABSTRACT

Purpose: Analyzing and observing the obtained multi-laminar structure of polymer nanocomposites performed by non-conventional technique of injection moulding.
Design/methodology/approach: Basing on DOE conventional technique was evolved and fitted out with additional mould externally operated by computer and pressure machine (generating 150 bar hydraulic pressure).
Findings: Chosen method brings advantage of final highly developed and reinforced structure during manufacturing.
Research limitations/implications: Polymer-layered silicate and silica nanocomposites are nowadays very important engineering materials showing their noticeable impact among composites.
Practical implications: Nanocomposites with created layered structure on nano and micro level are undoubtedly high performance engineering materials with promising growth and with continuous interests and developing branch in science and industry.
Originality/value: Non-conventional technique allows for the manipulation through reversing of the melted polymer and polymer blends while the cooling phase starts, creating self-reinforced polymer composite.
Keywords: Injection moulding; Polymer composites; Multilaminar structure; Silicates; Engineering materials

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1. Introduction

In nature nanostructures occur commonly. Many examples of biological micro and nanostructure systems like bones, sinews, cells, organs or tissues can be found. Equipped by nature, systems are manifold role models designed by engineers and architects. Macromolecules and biological molecules build nanostructures and nanocomposites in biological systems [1-6]. Based on these discoveries many composites (including laminate, dispersed and fibre morphology) are created. Polymer-layered silicate and silica nanocomposites are nowadays very important engineering materials showing their noticeable impact among composites [7-10]. However nanocomposites with created layered structure on nano level are undoubtedly composites of high performance with promising growth and with continuous interests [11-15], although composites with micro-sized structure are also interesting and simultaneously developing branch in science and industry [16-18]. There are many processes to obtain polymer composites, in which the following can be listed: moulding, thermoforming, coating, casting, expansion and others [19,20]. In each of these categories there are subcategories and different techniques. Laminated polymers, which are the subject of this paper, may be obtained as one of injection subcategory. [21]. Polymer composites since 1940's, when used for military and aerospace applications, offer many advantages comparing to conventional materials including lightweight, corrosion resistance, cheap and easy processing and wide range of applications from domestic use products, through structural composites, up to the high-tech composites used in the space and advanced industries [22-28]. The technique used to obtain final products should include a concept about manufacturing method, and used materials. In the paper a chosen method brings advantage of final structure preparation during manufacturing a part, making self-reinforced composite. Thanks to the applied forces, finally obtained multilaminar structure is highly developed and reinforced. In spite of many discoveries, composites are still an interesting topic in research.

2. Experimental

2.1. Specimens preparation

Polypropylene (PP) as base material has been used in this work. Material data is specified in the Table 1.

Before processing material was dried in a dehumidifier for 1 hour in 50ºC according to the supplier recommendations. No chemical pre-treatment and preliminary heat treatment was performed. All moulded specimens with rectangular bars shape assigned for fracture tests were prepared by direct injection moulding in a Ferromatik Milacron K-85 equipped with SCORIM head. The fracture tests were performed in a Instron 4505 universal testing machine at the crosshead velocity of 10 mm/min, accordingly to ASTM E399 norm. A notch 6.35 mm deep was made at a Ceast 6816 cutting machine with triangular blade with a 0.47 mm tip radius. Air humidity (50%) and air temperature (23ºC) were under stable conditions by sensor controlled system. Minimum of five specimens have been analysed for each test, giving at least 3 values per test, even extreme results are cut for proper estimation of average and standard deviation values.

2.2. Polarized light microscopy (PLM)

Thin slices of 20 µm cut on Microtom Anglia, were observed by polarized light on Olympus light microscope type BH2 additionally equipped with the Olympus digital camera DP11. This observation allowed for evaluation of microstructure, especially in analyzing and counting size and number of layers in the sheared multilaminar zone. High resolution of the photos was required for efficient recognition and counting the layers. Interactive image analyser computer software Quantimed 500ºC has supported image analysis.

2.3. Scanning electron microscopy (SEM)

Scanning electron microscope Leica Cambridge type S 360 at voltage of 15 kV was used to observe fracture surfaces perpendicularly to the flow direction after coating the broken specimens by a thin golden layer.

2.4. Technology

Injection moulding technique was used in the experiment. This conventional technique was evolved and fitted out with additional mould externally operated by a computer and a pressure machine (generating 150 bar hydraulic pressure). The machine, with computer aided system, controlled piston movements actuated by pressure transmitted trough pressure hoses to the mould, with second precision. This whole system was aimed at control flow of melt polymer reciprocation during solidification. Shear induced during this stage influences morphology and causes creation of multilayer zone. The number of layers is dictated by set of piston movements, namely by two parameters – number and time between feeds. The SCORIM stage (SCORIM - shear controlled orientation in injection moulding) operates 3 modes. Mode A and C were tapped in the processing. Mode A is the dynamic mode, where pistons are in concurrent strokes, actuated by hydrodynamic pressure (Fig. 1).

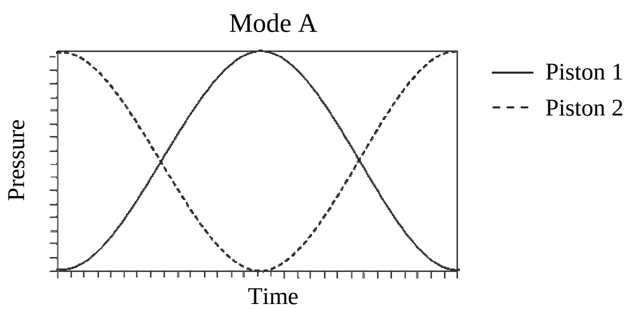

Fig. 1. Pressure profile in time function in the A cycle mode

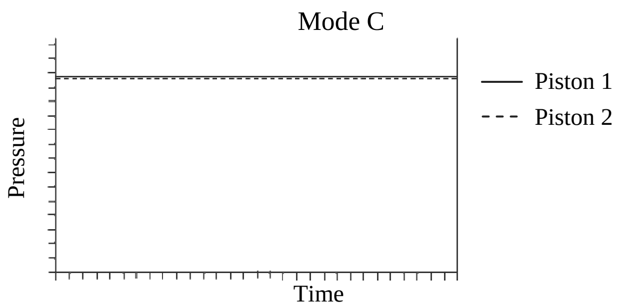

Fig. 2. Pressure profile in time function in the A cycle mode

Table 1.
Material specifications

Material	Grade	Supplier	Density	Volume flow index	Melt temperature
Polypropylene	Moplen HP 501M	Basell	0.9 g/cm^3	10 cm^3/10 min	200ºC

Mode C works with hydrostatic pressure, while pistons compact injected and formed material inside cavity to assure precise shaping and to avoid shrinkage (Fig. 2).

Main three processing settings, that is melting temperature, time of piston stroke and number of piston strokes where considered just in mode A. Mode C, where material was kept under stabilized pressure, excludes work of pistons, so just the melting temperature was the one variable parameter. This set-up was in principle the conventional injection moulding. The experiment made without SCORIM stage (moulding condition no. 9 and 10) was important as comparable testing representing a conventional technique. This allowed to make the statement between both techniques – conventional and non-conventional one.

To evaluate properly values, a logical experimental schedule was necessary to be compiled. In this experimental plan different variations for all parameters mutually collated have been considered (Table 2).

Table 2.
Two-level, three-factor Taguchi array (L8) of processing parameters

Moulding condition	Melting temp. *[ºC]*	Stroke time *[s]*	Stroke number
N-CIM 1	240ºC	1	3
N-CIM 2	280ºC	1	3
N-CIM 3	280ºC	1	12
N-CIM 4	240ºC	1	12
N-CIM 5	280ºC	3	3
N-CIM 6	240ºC	3	3
N-CIM 7	240ºC	3	12
N-CIM 8	280ºC	3	12
CIM 1	240ºC	-	-
CIM 2	280ºC	-	-

Eight experiments as result of mutual combinations of particular factors delivered complex of information about influence of processing on the morphological modifications. Conventional injection moulding (CIM) and non-conventional injection moulding (N-CIM) processes are mainly controlled by temperature of injected melting polymer, so this parameter has been taken into consideration as variable at two levels (Fig. 3).

Settings for both techniques are ordered according to shearing time, while flow was under shear (sum of injection time and SCORIM time). Low and high values were chosen for stroke time and stroke number as mostly representative values influencing final morphology (Fig. 4).

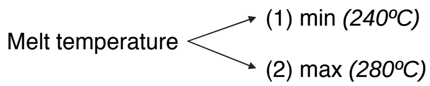

Fig. 3. Two levels for variable CIM and N-CIM parameter

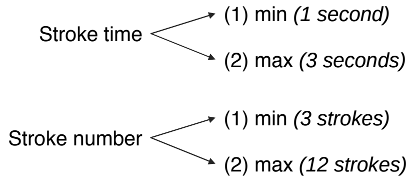

Fig. 4. Two levels for variable SCORIM parameters

One second was the minimum time between strokes possible to set. Higher value of stroke timing in the SCORIM process has been set for 3 seconds. This choice was dictated by choosing relatively short time of total process. CIM techniques characterizes creation of one skin layer in the structure at one side of the obtained mould. Three strokes as minimum number of strokes in N-CIM programme have been chosen to obtain more than one layer, influencing concurrently the structure. Similarly as for dependence between low and high values of established stroke time (1 and 3 seconds), stroke numbers have been fourfold multiplied between low and high value (3 and 12). Shear time is the result of multiplication of stroke time and stroke number. Each injecting process was finalized an equal set of mode C.

3. Results and discussion

Differences in processing have a great reflex on morphology. Control of timing and number of SCORIM factors brought satisfactory results and proved that through these actions structure substantially can be modified according to desired expectations.

Solidifying melt induces shear between particular layers, which are created by single stroke. Each stroke contributes to inception of new layer. Different timing between strokes gives different time for solidification between layer and influence on further development of the whole shearing zone.

Comparison of CIM and lowest stroke time-stroke number settings of N-CIM shows clearly change in the structure affected by N-CIM (Fig. 5, Fig. 6). SEM observation (Fig. 7) emerged very similar, homogenous surface. PLM image approved one layer morphology expected for this condition (Fig. 7). Ordinarily obtained structure in CIM with one outer skin layer was expected. Innovation in the form of SCORIM system yielded extended structure.

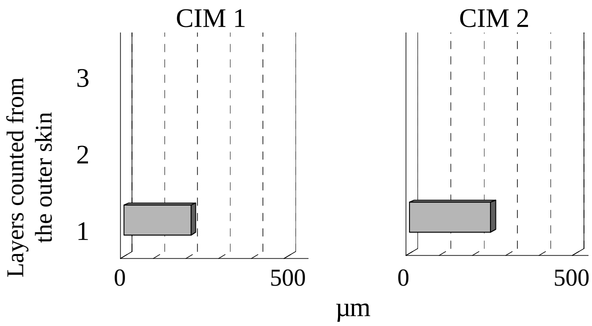

Fig. 5. Simile of two conditions of conventional technique

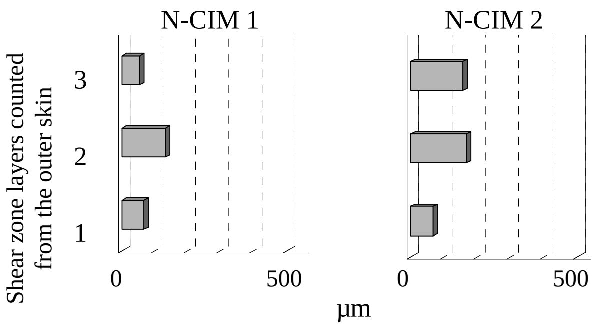

Fig. 6. Simile of four conditions, where shear zone is not highly developed

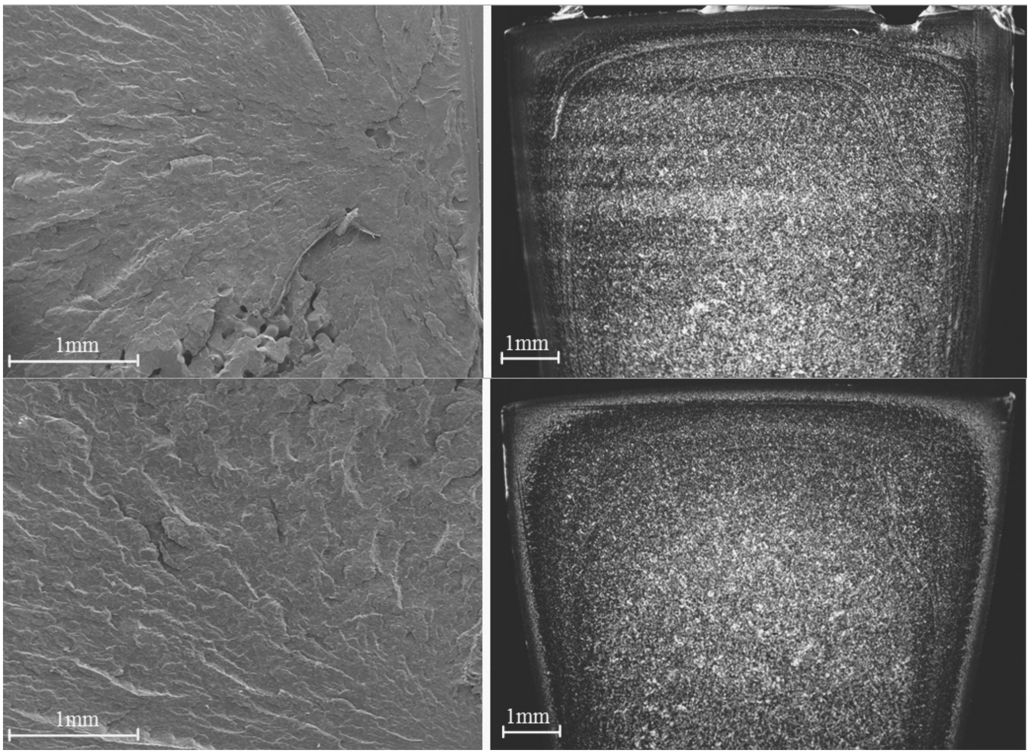

Fig. 7. SEM and PLM images of structures obtained by CIM, a) CIM 1, b) CIM 2

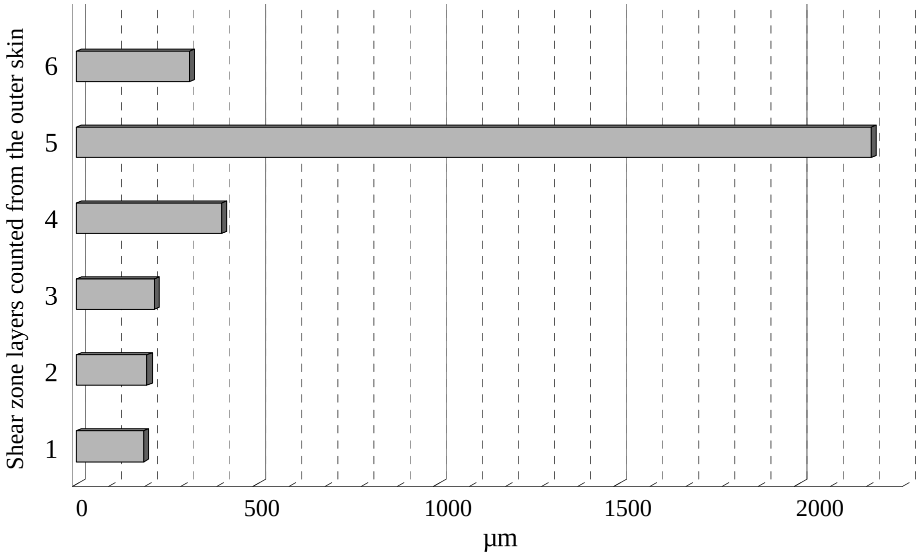

Fig. 8. Highly developed multilayer zone in N-CIM 3

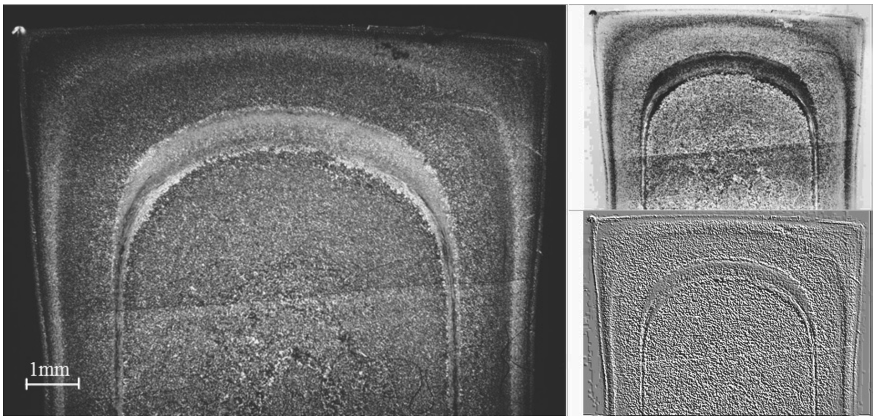

Fig. 9. On the left - PLM image of structure obtained by N-CIM 3, on the right – enhanced images for clarifying layers' visibility by some graphic tools (gamma correction, negative function, color balancing, embossing)

The first and second setting (N-CIM 1 processed at 240ºC and N-CIM 2 processed at 280ºC), where number of stroke were equal to 3, built also equal number of layers (the outer one like in the CIM technique and two more). Short time between strokes (1s) did not create thick outer layer (just 67 µm, comparing to CIM where 206 and 245 µm, respectively). Second and third layer were thicker for material processed at higher temperature. It could happen due to lower viscosity, which allowed for better flow of the melt and due to slower cooling rate. Next condition (N-CIM 3), according to experimental table with fourfold multiplied number of stroke, changed structure drastically (Fig. 8, Fig. 9) comparing to N-CIM 1 and N-CIM 2 described above.

Change of temperature at the same level of stroke time (1s) and number of strokes (12) extended structure and 7-layer sector has been created. During several movements particular layers were "erased" by sequential melt flow. Short time between strokes influenced gradientaly layered composition (Fig. 10). To have clearly legible measurements of layers, e.g. local balancing of colour palette is supported by image analyzer and image enhancing tools. Thanks to these operation, boundaries of layers were sharpen and easy to determine. Two pairs of settings for two temperatures brought adequate results. Setting N-CIM 5 (Fig. 11, Fig. 12) and N-CIM 6 is characterized by 3-layer sectors (Fig. 13, Fig. 14). Both conditions, where number of strokes was 3 and time of stroke was 3s, contain thin outer layer (300 and 118 µm respectively) comparing to the other two. Lower temperature beneficially influenced on the layers' growth. However, thick layers in the N-CIM 5 did not reinforce structure as good as thinner layers in N-CIM 6, where fracture energy needed to break the specimen were almost doubled (detailed information about mechanical tests will be published in the subsequent publication). Comparison of all conditions accordingly to layers development due to processing parameters is presented on Fig. 15.

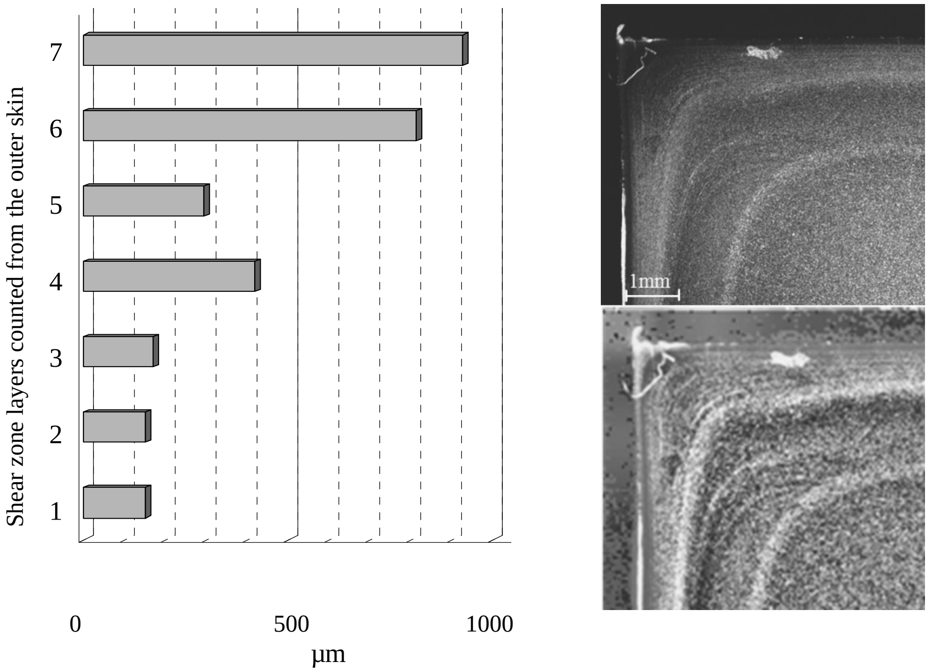

Fig. 10. Highly developed multilayer zone in N-CIM 4, left figure shows measurement of layers, right figure exhibits PLM image with clearly visible multilayer structure; for better evaluation, some images were digitally enhanced by advanced image software

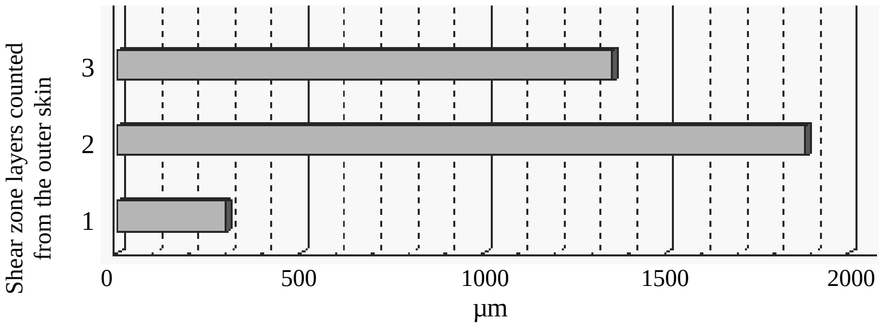

Fig. 11. Multilayer zone for N-CIM 5

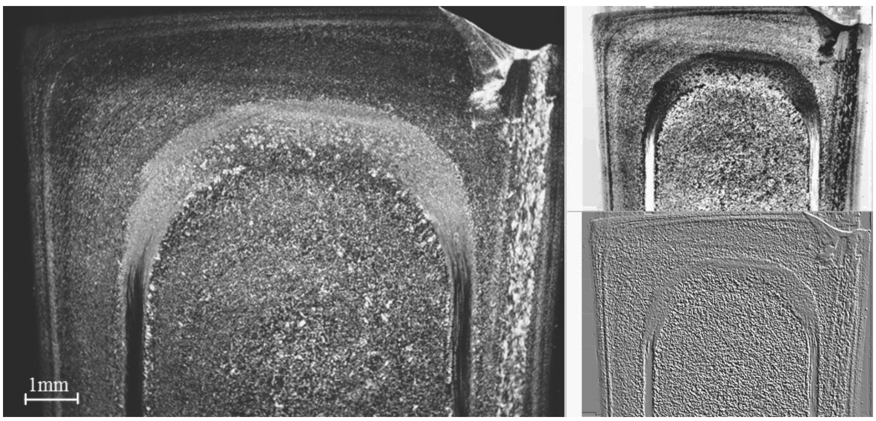

Fig. 12. On the left - PLM image of structure obtained by N-CIM 5, on the right – enhanced images for clarifying layers' visibility by some graphic tools (gamma correction, negative function, color balancing, embossing)

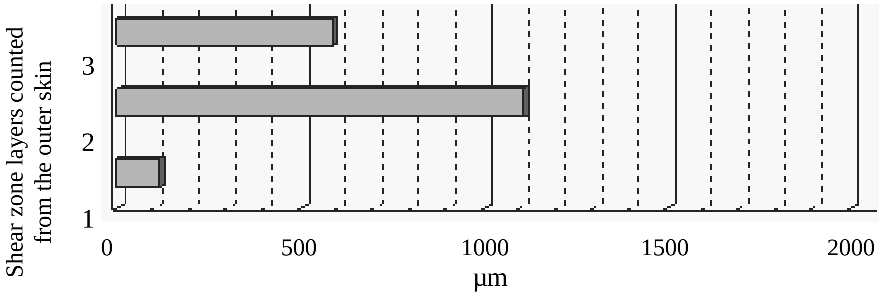

Fig. 13. Multilayer zone for N-CIM 6

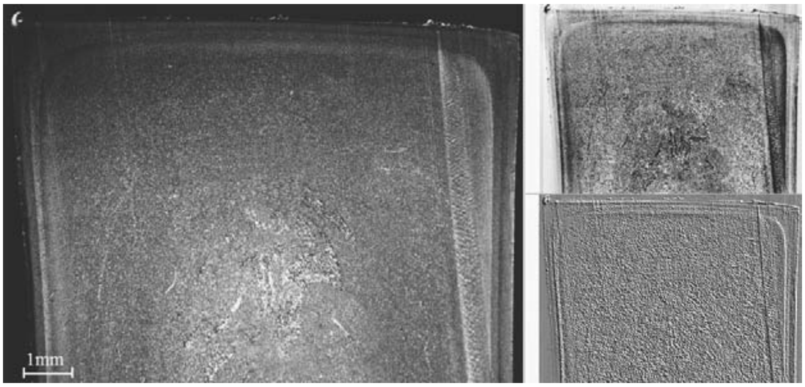

Fig. 14. On the left - PLM image of structure obtained by N-CIM 6, on the right – enhanced images for clarifying layers' visibility by some graphic tools (gamma correction, negative function, color balancing, embossing)

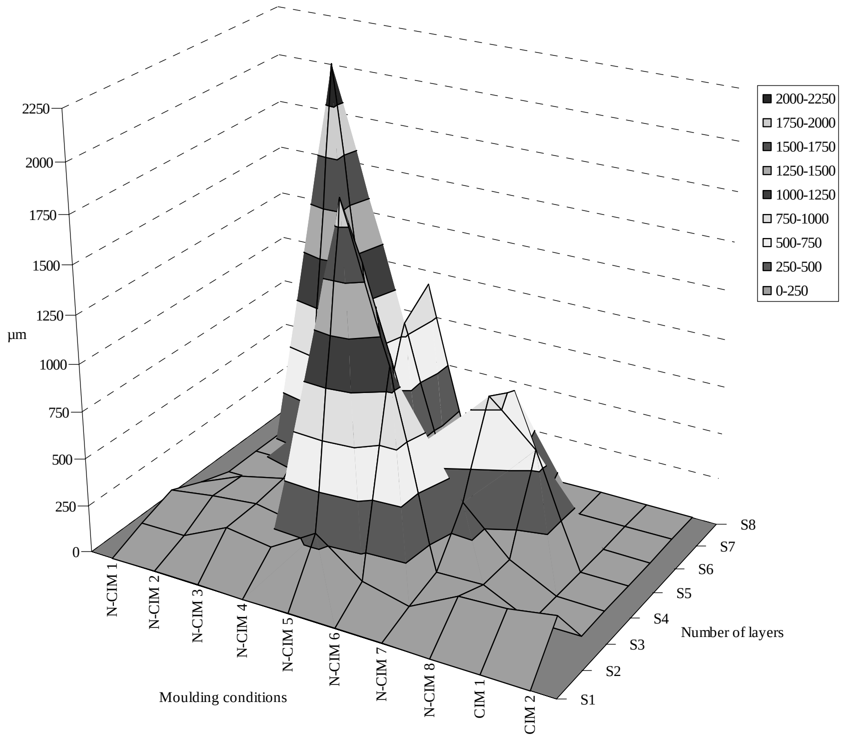

Fig. 15. Comparison of layers development due to processing conditions

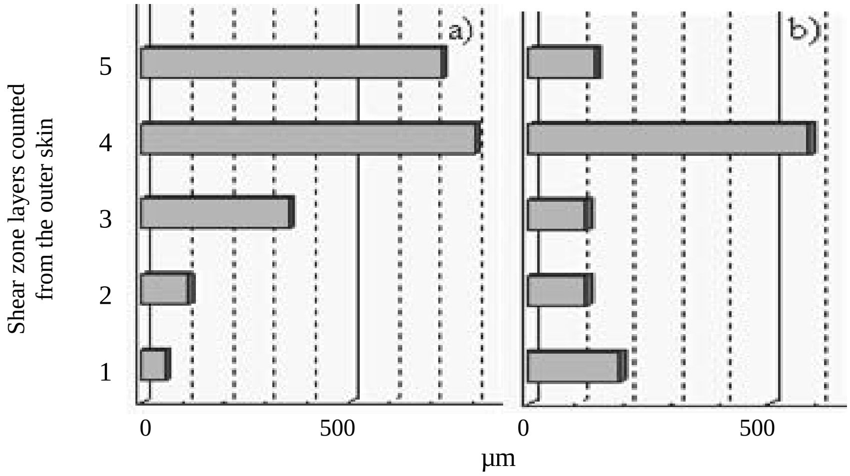

Fig. 16. Multilayer zone for a) N-CIM 7 and b) N-CIM 8

The last two diagrams (Fig. 16) display difference for N-CIM 7 and N-CIM 8. In these conditions maximum of all settings were used (12 strokes and 3s of stroke time), what in effect created 5-layer zones with thin outer layers. Fourth layer for both temperatures developed visibly and the last one developed just in lower temperature. The longest time of total process and low temperature allowed the melt to solidify faster and the last layer frozen with the thickness of 727 µm, which is 6 times more than fifth layer obtained in higher temperature.

4. Conclusions

Constitutive summary of the analyzed self-reinforced composites modification of injection moulding technique and use of additional post-injection stage found meaningful application. Modification of processing set-up reflex on final morphology of performed composites. Controlling parameters SCORIM, namely confluence of number and time of strokes can be designed by microarchitecture of composites, and thereupon influence on mechanical properties and their improvement. Structures obtained by this technique where much more developed also with gradient character of layers' construction.

Thickness of layers not always is adequate to the stiffness of produced elements, which will be explained in the next publication, however reinforcement of structure can be reported, especially comparing to the CIM. This technique used for thermoplastics, in this experiment for the PP, is very promising against the rising importance induced by the rapid development of nanoscience and nanotechnology. Galleries of nanoparticles can be easily broken thanks to high shear rates in the flow orientation during strokes [4], so the technique can be efficiently used to obtain high performance nanocomposites without pre-treatment. Manufacture of thin polymer layers by SCORIM technique is thus imperative step for the polymer composite advancement with ability of morphology control and potential to obtain expected properties.

References

[1] R.A. Sousa, R.L. Reis, A.M. Cunha, M.J. Bevis, Processing and properties of bone-analogue biodegradable and bioinert polymeric composites, Composites Science and Technology 63 (2003) 389-402.

[2] Y.C. Ke, P. Stroeve, Polymer-Layered Silicate and Silica Nanocomposites, Elsevier, 2005.

[3] C.M. Niemeyer, Nanoparticles, proteins, and nucleic acids: biotechnology meets materials science, Angewandte Chemie-International Edition In English 40/22 (2001) 4128-4158.

[4] U. Drechsler, B. Erdogan, and V. M. Rotello, Nanoparticles: Scaffolds for molecular recognition, Chemistry - A European Journal 10/22 (2004) 5570-5579.

[5] T.E. McKnight, A.V. Melechko, G.D. Griffin, M.A. Guillorn, V.I. Merkulov, F. Serna, D.K. Hensley, M.J. Doktycz, D.H. Lowndes, M.L. Simpson, Intracellular integration of synthetic nanostructures with viable cells for controlled biochemical manipulation, Nanotechnology 14/5 (2003) 551-556.

[6] G.A. Silva, Nanotechnology approaches for the regeneration and neuroprotection of the central nervous system, Surgical Neurology 63 (2005) 301-306.

[7] S.S. Ray, M. Okamoto, Polymer/layered silicate nanocomposites: a review from preparation to processing, Progress in Polymer Science 28 (2003) 1539-1641.

[8] L.A. Dobrzański, M. Bilewicz, J.C. Viana, A.M. Cunha, Non-conventionally obtained polymer nanocomposites at different nano-clay ratios, Journal of Achievements in Materials and Manufacturing Engineering 31/2 (2008) 9-14.

[9] M. Bilewicz, J.C. Viana, L.A. Dobrzański, Development of microstructure affected by in-mould manipulation in polymer composites and nanocomposite, Journal of Achievements in Materials and Manufacturing Engineering 31/1 (2008) 71-76.

[10] A. Pozsgay; T. Fráter; L. Papp; I. Sajó; B. Pukánszky, Nucleating Effect Of Montmorillonite Nanoparticles In

Polypropylene, Journal of Macromolecular Science B 41/4-6 (2002) 1249-1265.
[11] R. Nowosielski, J. Wysocki, I. Wnuk, P. Sakiewicz, P. Gramatyka, Ferromagnetic properties of polymer nanocomposites containing $Fe_{78}Si_9B_{13}$ powder particles, Journal of Achievements in Materials and Manufacturing Engineering 13 (2005) 493-496.
[12] J.M. Torralba, C.E. da Costa, F. Velasco, P/M aluminum matrix composites: an overview, Journal of Materials Processing Technology 133/1-2 (2003) 203-206.
[13] M. Zenkiewicz, J. Richert, Influence of polymer samples preparation procedure on their mechanical properties, Journal of Achievements in Materials and Manufacturing Engineering 26/2 (2008) 155-158.
[14] N. Anyadike, Small Beginnings, Flexible 6 (2003) 6-14.
[15] D.L. Hunter, French Montmorillonite For Plastic Reinforcement, Composites International English 53 (2002) 85-86.
[16] T.J. Reinhart, Introduction to Composites in Engineered Materials, Handbook, ASM International, 1987.
[17] T.J. Reinhart, Overview of composite materials in S.T. Peters, Handbook of Composites, Chapman & Hall, London, 1999.
[18] W. Brostow, Properties of polymer liquid crystals: choosing molecular structures and blending, International Journal for the Science and Technology of Polymers 31/6 (1990) 979-995.
[19] W. Watt, B.V. Perov, Handbook of Composites, Vol. 1: Strong Fibres, Amsterdam, North-Holland, 1985.
[20] S.W. Tsai, Composites Design 1986, Dayton, OH: Think Composites, 1986.
[21] G.H. Staab, Laminar Composites, Butterworth-Heinemann, 1999.
[22] L.A. Dobrzański, Fundamentals of Materials Science and Metallurgy. Engineering Materials with fundamentals of Materials Design, WNT, Warsaw, 2002 (in Polish).
[23] D. Short, J. Summerscales, Hybrids - A Review, Part 2. Physical Properties, Composites 11 (1980) 33-40.
[24] B.T. Åström, Manufacturing of Polymer Composites, Chapman & Hall,1997.
[25] R.A. Freitas Jr., Nanomedicine, Volume 1: Basic Capabilities, Landes Bioscience, Austin, 1999.
[26] B. Cavalcanti, R.A. Shirinzadeh, Jr. Freitas, L.C. Kretly, Medical Nanorobot Architecture Based on Nanobioelectronics, Recent Patents on Nanotechnology 1/1 (2007) 1-10.
[27] K.L. Ekinci, M.L. Roukes, Nanoelectromechanical systems, Review of Scientific Instruments 76 (2005) 061101.
[28] J.H. Koo, Polymer nanocomposites. Processing, characterization and application, McGraw-Hill, 2006.