Influence of phyllosilicates 2:1 on structure of polymer nanocomposites

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Manufacturing and processing

ABSTRACT

Purpose: To verify influence of nanoparticles on structure development.

Design/methodology/approach: Injection moulding technologies including conventional and non-conventional ones.

Findings: Stiffness of materials reinforced by MMT increased dramatically and expectations of most interesting results were concentrated close to 3 wt% of nano filling.

Research limitations/implications: N-CIM technology allows control of development of the structure, limited by parameters of non-conventional injection system (time, pressures etc).

Practical implications: PP/MMT nanocomposites are the promising engineering materials with wide range of application for household equipment, agriculture, packaging, medicine, automotive and building engineering.

Originality/value: Induced shearing supports splitting of agglomerations, improve dispersion and intercalation of MMT. Better distribution improves significantly the strength.

Keywords: Polymer processing; Engineering materials; MMT; Polymer nanocomposites

1. Introduction

Nowadays needs of market, advanced applications, development of different domains e.g. engineering materials for construction, automotive and aviation components, sport equipment or medicine destination, force industry R&D centers and academic laboratories to search for possibilities how to improve properties of materials, search for new properties and materials or modify existing ones. Focusing any domain, like e.g. sport discipline or any nowadays produced cars, there is always a lot of research behind the final product, and computer aided engineering is fully explited [1-3]. To gain a victory in any sport discipline or in production of new vehicles, both driving and flying ones, the necessary condition is to use available or design new material with superior properties, mostly low weight and

high strength. The key to the success is the material. Material engineering, basing on knowledge of chemistry and physics, and as well as knowledge about main engineering materials like metal, ceramic and polymer and mutual composition of them, is then most suitable direction to develop and obtain such awaited materials with excessive properties. Composites are the materials that are using properties of several basing materials and expand the range of possible applications. Next step in composing of materials are nanocomposites, which use power of nanotechnology and expand further scope of applications. Research over properties of different materials, understanding and design of new manufacturing technology or development of existing ones, assortment of materials is just the beginning of research, because the properties of any material depend on its matter, with which it is created, as well as arrangement of the atoms it's made of. Change of properties can be then made on

nano or micro level, often more effective for the changes done at lower, molecular level. Even just use of nanoparticles is very often the way providing to satisfactory results. Composites and nanocomposites are then both commercially used and future materials which are still under investigation and continuous development. Considering significant interest in polymers (Fig. 1), can be concluded, that polymers and basing on polymer matrix nanocomposites as an economic, interesting and very promising class of polymer composites, derived from nano-scale particles, are investigated worldwidely, signifying broad scope of material composition possibilities (Fig. 2) [4-11].
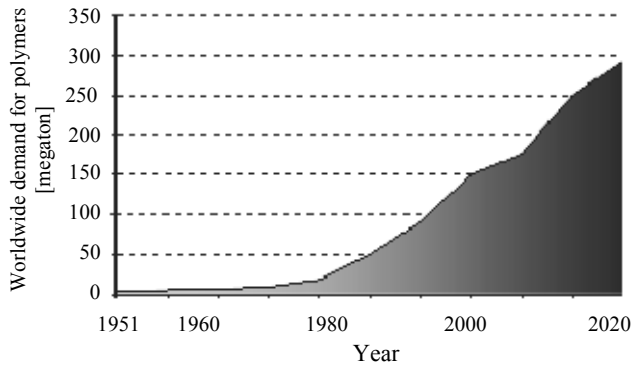

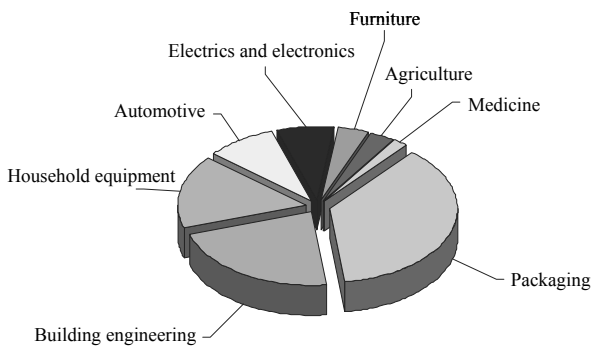Fig. 1. Worldwide demand for polymeric materials [12]

Fig. 2. The percentage contribution of polish industries that use polymeric materials [13]

Expanding production and human needs contribute to the rising consumption per capita which reaches level of 120 kg for East Europe (Fig. 3).

Control of manufacturing process may influence on structure creation. Manufacturing can be done in conventional way or by non-conventional techniques. The second one is the response to the search for better and promising materials. Focusing on polymeric materials and their composites and nanocomposites among many technologies of manufacturing, most known and commercially used are:

- Extrusion;
- Injection blow molding;
- Reaction Injection Molding (RIM);
- Reinforced Reaction Injection Molding (RRIM);
- Rotational molding;
- Co-injection Molding;
- Expansion bead molding;
- Extrusion blow molding;
- Turret Molding;
- Fluidized bed;
- Gas Assisted Injection Molding (GAIN);
- Forging;
- Compression molding;
- Powder Injection Molding;
- Liquid resin molding techniques (LRM);
- Resin transfer molding (RTM);
- Vacuum injection molding (VIM);
- Thermal-expansion resin transfer molding (TERTM);
- Spray-up molding;
- Structural foam molding;
- Sheet thermoforming;
- Vacuum forming;
- Pressure forming;
- Trapped sheet forming;
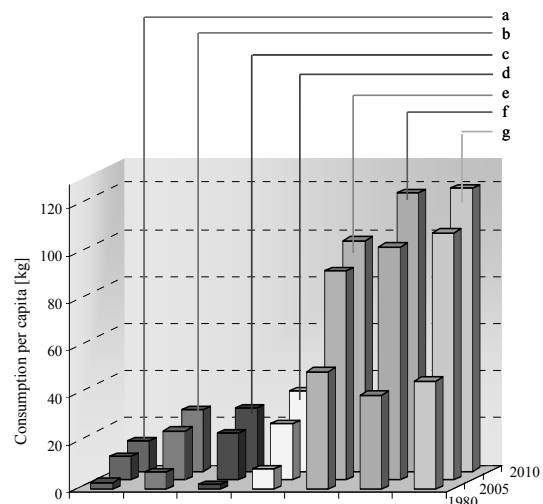- Steam pressure forming.

Fig. 3. Consumption of polymeric materials per capita for different regions; a - Middle East and Africa, b - Latin America, c - Asia without Japan, d - Central and Eastern Europe, e - Japan, f - Western Europe, g - NAFTA (North American Free Trade Agreement) [14]

Non-conventional techniques adapt technology and machinery to necessity of materials. Among these techniques of processing of polymeric materials can be mentioned:

- Compression injection;
- Moving boundary technique;
- Low pressure injection moulding;
- Spin injection;
- Vibration-assisted injection moulding;
- Vibration moulding;
- Rheomoulding;
- Vibrated gas-assist moulding.

Application of products obtained by conventional and non-conventional injection moulding, also with use of rotational or multicavity moulds, starts at domestic level of products and finishes with advanced engineering nanocomposites. Solidifying polymer subjected to flow inside mould cavity, during its crystallizing and solidifying phase and undergoes to high shear rates, creates developed structure with multilayer zone, more oriented than structure obtained by conventional injection moulding process (Fig. 4).
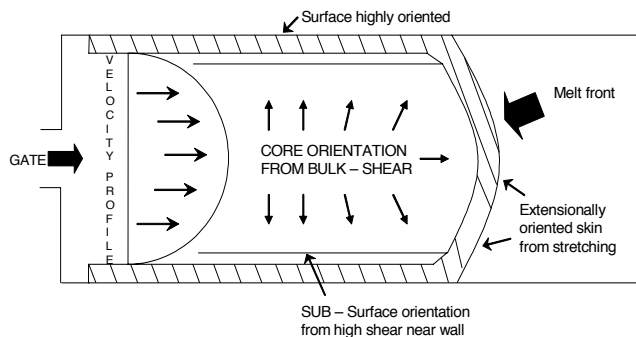

Fig. 4. Melt flow profile during injection

During processing such as extrusion or injection molding molten polymers are subjected to flows and in the case of semicrystalline polymers, as PP, crystallization process appears during the flow, and the properties are strongly influenced by the final crystalline structure on properties may drastically increase, thanks to reduction of segmental mobility of molecular chains in the inner spherulite amorphous regions of a polymer, which provide to the increase of the mechanical properties [15-22].

Control of the processing and creation of the designated structure is one direction. The other direction is control of ratio of mixed materials, their type, particle size and particle shape. Among many reinforcing materials, for special attention deserve nanosized particles. It has been notified, that nanoclay may affect morphology on molecular level and drastically improve properties of polymer composites [4,10,11,20].

Shape of particles determines properties of material and its destination of working environment, so the particles are selected dependently to requirements and the shape of particles can be chosen accordingly to their shape ratio (Table 1).

Table 1.
Shape of reinforcing particles

Shape				
	Spherical	Solid	Platelet	Fibrous
Shape ratio	1	1-4	5-100	>10
Example	Glass spheres	Calcium carbonate	Mica Graphite	Carbon fibres Glass fibres

In this work attention was given to particles with platelet shape, suitable for containers where gas barrier is needed for preventing transmission of gas through membranes, and also suitable for composites to increase stiffness and resistance for bending. From the smectite group of platelet particles, one of most representative is montmorillonite with layered structure basing on one internal octahedral sheet and two tetrahedral on both sides of internal one, in abbreviation called clay with structure 2:1, containing atoms of aluminum, silica and magnesium, described by formula: $Mx(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4AlO_6$ (Fig. 5).

Montmorillonite belongs to smectite group, where can be specified also other materials (Table 2) [23-29].
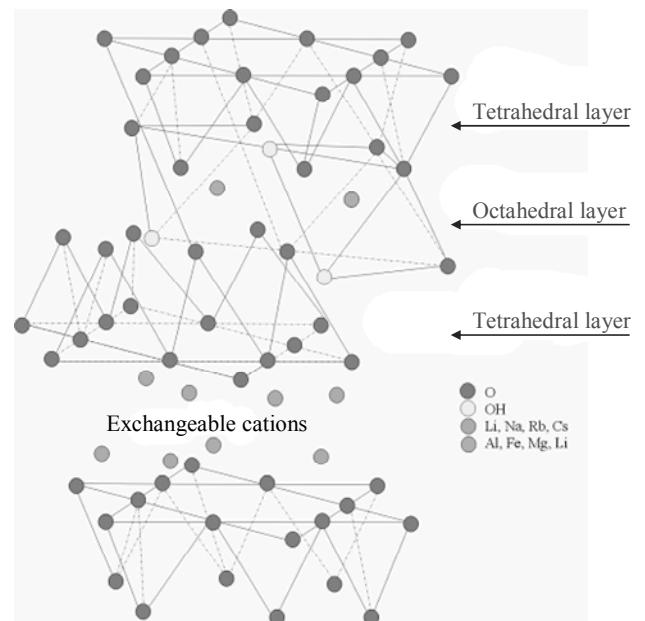

Fig. 5. Schematic illustration arrangement of atoms in a montmorillonite layer

2. Materials and methods

To obtain nanocomposites were used two materials, one was used as matrix and second one as reinforcement. For the matrix was chosen isotactic polypropylene HP501 (PP) from Bassell (Fig. 6), commercially available and economic thermoplastic polymer, rugged and resistant to numerous chemical solvents and acids.
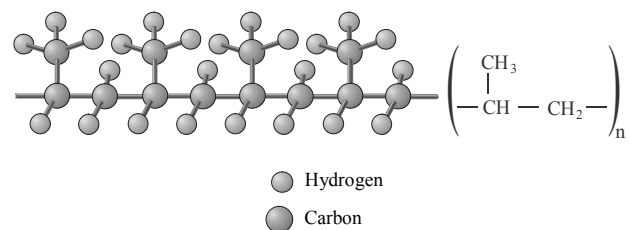

Fig. 6. Structure of isotactic polypropylene

Table 2
Materials from smectite group and their formulas

Material	Formula	Specification
Aliettite	$Ca_{0.2}Mg_6((Si, Al)_8O_{20})(OH)_4 \cdot 4H_2O$	Sheets of 6-membered rings interlayered 1:1, 2:1, and octahedral, monoclinic
Beidellite	$(Na,Ca_{0.5})_{0.3}Al_2((Si, Al)_4O_{10})(OH)_2 \cdot nH_2O$	Sheets of 6-membered rings with 2:1 clays, monoclinic
Ferrosaponite	$Ca_{0.3}(Fe^{2+}, Mg, Fe^{3+})_3((Si, Al)_4O_{10})(OH)_2 \cdot 4H_2O$	Phyllosilicates with mica sheets, monoclinic
Hectorite	$Na_{0.3}(Mg, Li)_3(Si_4O_{10})(F, OH)_2$	Phyllosilicates with mica sheets, monoclinic
Nontronite	$Na_{0.3}Fe_2((Si, Al)_4O_{10})(OH)_2 \cdot nH_2O$	Phyllosilicates with mica sheets, monoclinic
Pimelite	$Ni_3Si_4O_{10}(OH) \cdot 4H_2O$	Sheets of 6-membered rings with 2:1 clays, hexagonal
Saliotite	$(Li, Na)Al_3(AlSi_3O_{10})(OH)_5$	Sheets of 6-membered rings interlayered 1:1, 2:1, and octahedral, monoclinic
Saponite	$Ca_{0.25}(Mg, Fe)_3((Si, Al)_4O_{1-})(OH)_2 \cdot nH_2O$	Sheets of 6-membered rings with 2:1 clays, monoclinic
Sauconite	$Na_{0.3}Zn_3((Si, Al)_4O_{10})(OH)_2 \cdot 4H_2O$	Sheets of 6-membered rings with 2:1 clays, aluminosilicates of Mg, monoclinic
Swinefordite	$Li(Al, Li, Mg)_4((Si, Al)_4O_{10})_2(OH, F)_4 \cdot nH_2O$	Sheets of 6-membered rings with 2:1 clays, aluminosilicates of Li, monoclinic
Volkonskoite	$Ca_{0.3}(Cr, Mg, Fe)_2((Si, Al)_4O_{10)(OH)}2 \cdot 4H_2O$	Sheets of 6-membered rings with 2:1 clays, aluminosilicates of V and Cr, monoclinic
Zincsilite	$Zn_3(Si_4O_{10})(OH)_2 \cdot 4H_2O$	Sheets of 6-membered rings with 2:1 clays, Silicates of Ba, Sr and Zn, monoclinic

As reinforcement was used montmorillonite (MMT), compact earthy massive mineral with basal spacings sensitive to interlayer hydration and platelet structure (Fig. 7).
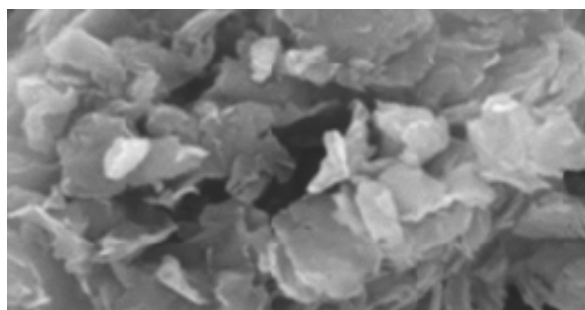

Fig. 7. Agglomerated, platelet structure of montmorillonite

Organic modification through exchange of cations, affects spacing, improve wettability and reduce superficial free energy; what ameliorate dispersion of MMT plates. Addition to the matrix was done at different ratio (Table 3).

Injection moulding was used in the research as common technique for processing polymers. Adaptation of the mould to non-conventional one, made possible develop structure from skin-core, typical for conventional injection moulding, to skin-multilayer-core, thanks to reciprocation of solidifying polymer inside cavity of the mould. During melting of polymer and mixing with nanoparticles, accompanying the process of injection moulding, polymer chains diffuse into the space between the intercalated galleries of montmorillonite.

Table 3.
Relative amount of components in investigated nanocomposites

Nr	Designation	MMT [wt%]	PP [wt%]
1	Neat PP	-	100
2	PP/MMT 0.5	0.5	99.5
3	PP/MMT 1	1	99
4	PP/MMT 3	3	97
5	PP/MMT 5	5	95
6	PP/MMT 10	10	90

Basing on design of experiment, polypropylene was blended with MMT at different ratio and parallely parameters of injection moulding also were set as low and high value. Finally were then compared five different nanocomposites with variable ratios PP/MMT for ten different combinations of flow parameters, what summarizing, finally gave sixty different nanocomposites (Table 4).

Low and high values for parameters were set as possible minimum equal to 1 second (St) of interval for stroke time and minimum equal to 3 strokes (Sn) as minimum required to obtain structure more developed (with minimum 3 layers in multilayer zone) than by conventional technique. Maxima were set for stroke time and stroke number as maximum of full time of processing (in the case of higher number time of processing and cooling of specimen was too long and in effect not economic and secondly solidification of polymer appears so creation of higher number of layers was difficult) (Table 5). Two modes of working of the non-conventional mould were basing on reciprocation and constant pressure (Figs. 8, 9).

Table 4.
Sets of parameters for non-conventional and conventional injection moulding technique

	CIM		N-CIM							
Set	1	2	1	2	3	4	5	6	7	8
Tm	1	2	1	1	1	1	2	2	2	2
St	-	-	1	2	1	2	1	2	1	2
Sn	-	-	1	1	2	2	1	1	2	2

where "1" means low value and "2" means high value of particular parameter (Tm, St, Sn)

Table 5.
Set of variable and constant parameters for processing by N-CIM technique

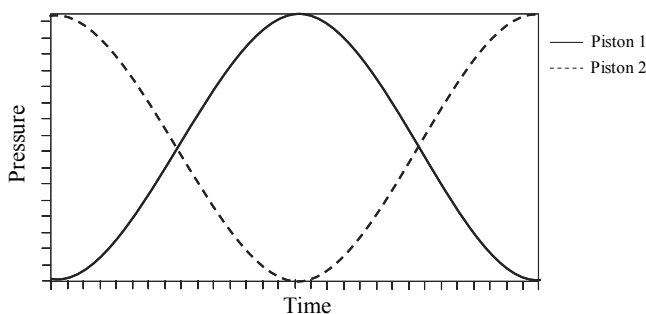| N-CIM		
Mode A (reciprocation)	Varied parameters	
	Melt temp. (Tm) [°C]	1	2
	Stroke time (St) [s]	1	3
	Stroke number (Sn)	3	12
Mode C (holding)	Constant parameter	
	Cooling time [s]	30

Fig. 8. The first mode of working of non-conventional mould - alternating movement - extension and retraction
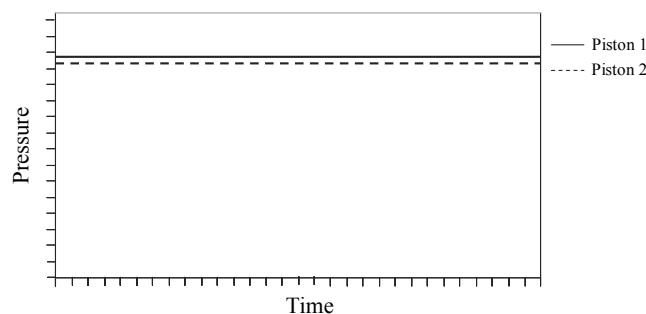

Fig. 9. The second mode of N-CIM process - constant pressure

Injection moulding process was controlled through control of most significant parameters, that is melt temperature of the polymer, common for conventional and non-conventional technique and stroke time and stroke number. Stroke means movement of two pistons simultaneously from top to down or from down to top. During this movement, one layer can be performed inside the cavity, with rectangular shape of specimen due to flow of melt polymer in one direction, cooling by contact with outer part of specimen, be contacted with wall of the mould, continuously cooled by water, and solidifying. Next movement of pistons creates another layer, which also solidifies and in this way is created multilayer zone between outer skin and inner core. High shear rate, accompanying flow of forced polymer, influence on high orientation of the created layer and influence on shattering of MMT agglomerates, improving intercalation and diffusion of polymer into space between MMT galleries.

Methodology of preparation specimens was divided for specimens for mechanical test and specimens for microscopic observation. Specimens obtained directly after injection moulding, when ejectors removed specimens from the cavity, were tested by 3-point bending test with crosshead speed 10 mm/1 (according to the ASTM E399standard) at controlled room temperature (23ºC). Fractured specimens were tested on the universal testing machine Instron type 4505, previously notched in a Ceast notch cutter type 6816 with a notch depth of a = 6.35 mm and then sharpened with razor blade.

Morphology of blends has been observed in polarized light, where light from a source passes polarizer and changes on plane polarized light and then crosses birefringent specimen, where light rays are split and nextly recombined passing through analyzer. Thanks to this technique isotropy and anisotropy of material is visible bringing more information about the structure, especially are revealed details of flow during injection and during reciprocation (clearly visible multilayer zone). Cross sections were chosen from the middle regions of specimens. Slices of 20 µm thick have been performed on the cut machine Microtom Anglia Scientific until suitable quality of a surface for microscopic observation was achieved. Specimens have been observed by polarized light microscopy and electron scanning microscopy in the aim to understand the structure development.

3. Results

Nanosized particles strengthen structure increasing the stiffness and toughness and these properties increase together with increment of nanofiller content up to 5 wt%. The testing of strength properties were carried out in order to check absorbed energy by the action of lateral force on the sample as a function of contribution of nanoparticles and to determine flexural strength. Results of testing of PP and nanocomposites are listed in the tables and figures below (Tables 6-11, Figs. 10-23).

Nanocomposites with 0.5% contribution of MMT particles, processed by CIM under low and high temperature, contain similar structure to neat PP, obtained under same condition (Tables 6 and 7, Figs. 10-13).

Table 6.
Flexural strength of PP [MPa]

Process	Set	Statistical values		
		Arithmetic average σ_{max} [MPa]	Standard deviation	Confidence interval min-max
CIM	1	36.40	1.66	36.04-37.13
	2	38.94	1.78	38.55-39.72
N-CIM	1	29.74	1.36	29.44-30.33
	2	30.79	1.40	30.48-31.41
	3	34.90	1.59	34.55-35.60
	4	47.56	2.17	47.09-48.51
	5	22.64	1.03	22.41-23.09
	6	26.14	1.19	25.88-26.67
	7	37.78	1.72	37.41-38.54
	8	42.45	1.94	42.02-43.30

Table 7.
Flexural strength of PP/MMT 0.5 [MPa]

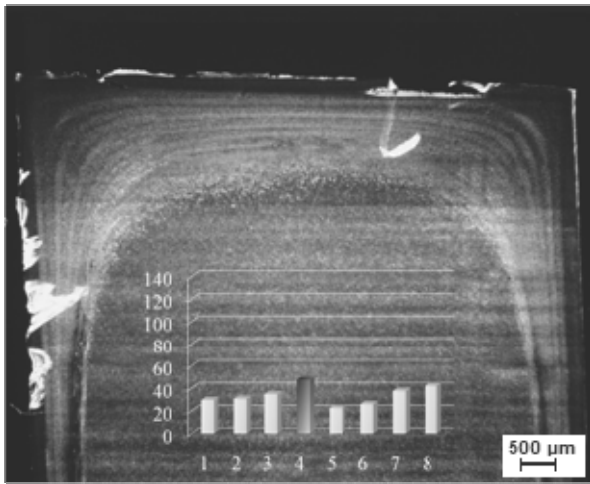| Process	Set	Statistical values		
		Arithmetic average σ_{max} [MPa]	Standard deviation	Confidence interval min-max
CIM	1	45.55	2.08	45.09-46.46
	2	50.51	2.30	50.01-51.52
N-CIM	1	50.42	2.30	49.92-51.43
	2	51.08	2.33	50.57-52.10
N-CIM	3	52.38	2.39	51.85-53.43
	4	66.78	3.05	66.11-68.12
N-CIM	5	58.17	2.65	57.59-59.34
	6	62.23	2.84	61.61-63.47
	7	62.09	2.83	61.47-63.33
	8	68.49	3.12	67.80-69.86

Fig. 10. Structure with visible multilayer zone of neat PP performed under condition of N-CIM equal to Tm/St/Sn 240/3/12; cross section was chosen from the middle part of specimen

Fig. 12. Structure with visible multilayer zone of PP/MMT 0.5 performed under condition of N-CIM equal to Tm/St/Sn 240/3/12; cross section was chosen from the middle part of specimen

Fig. 11. Structure with visible multilayer zone of neat PP performed under condition of N-CIM equal to Tm/St/Sn 280/3/12; cross section was chosen from the middle part of specimen
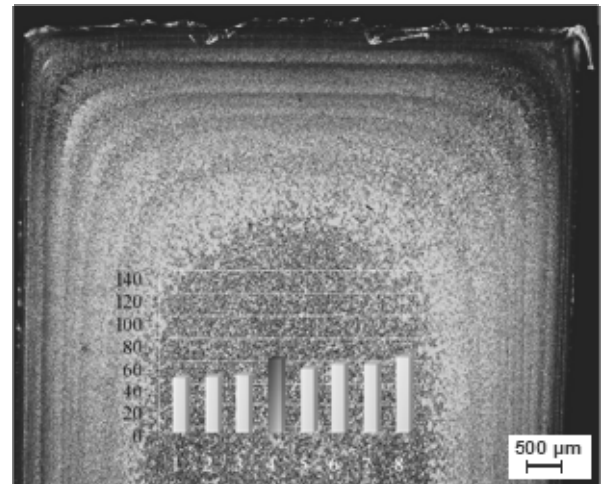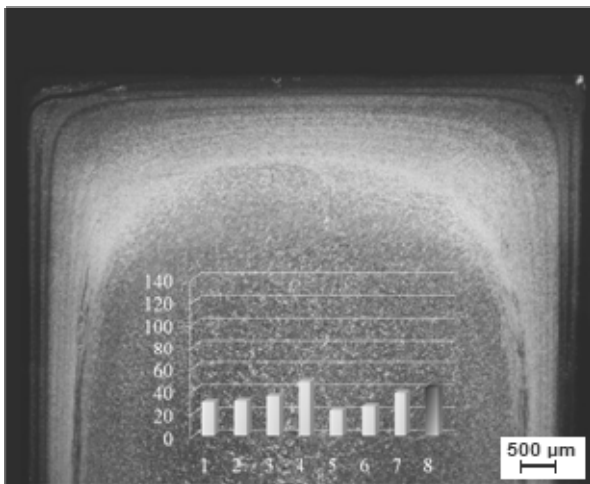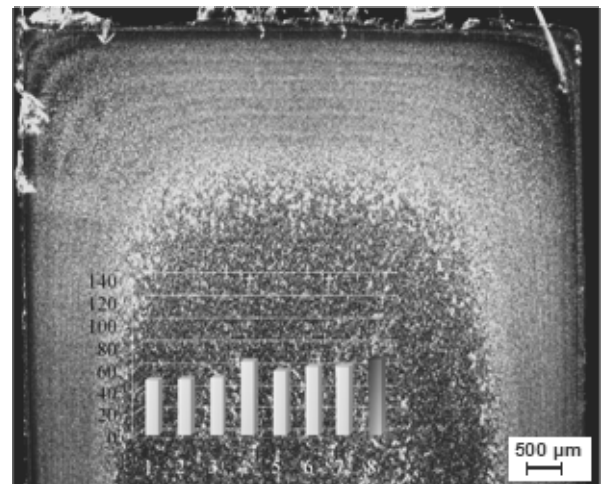

Fig. 13. Structure with visible multilayer zone of PP/MMT 0.5 performed under condition of N-CIM equal to Tm/St/Sn 280/3/12; cross section was chosen from the middle part of specimen

Forces during reciprocal movement of melt polymer during N-CIM process, formed multilayer zone, with the average layer thickness of 220 μm, where stroke number was set at maximum level. Increment of contribution of nanoparticles from 0.5 to 1 wt% didn't improve too much flexural strength and contribution of shear zone increased especially for the last set with parameters 280/3/12 (Table 8, Fig. 14).

Table 8.
Flexural strength of PP/MMT 1 [MPa]

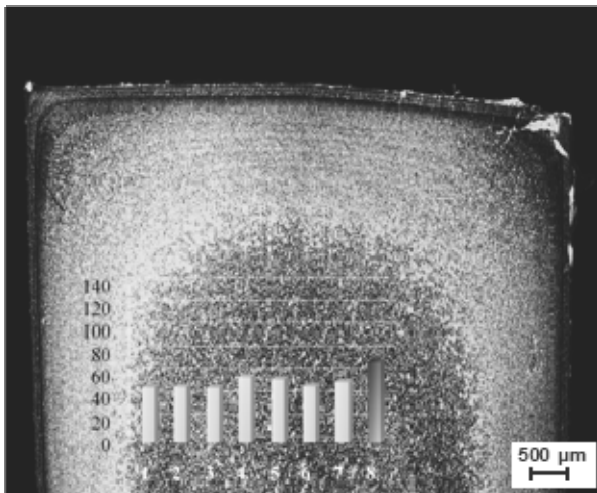| Process	Set	Statistical values		
		Arithmetic average σ_{max} [MPa]	Standard deviation	Confidence interval min-max
CIM	1	41.20	1.88	40.79-42.03
	2	41.14	1.88	40.73-41.96
N-CIM	1	48.25	2.20	47.76-49.21
	2	48.65	2.22	48.17-49.63
	3	47.84	2.18	47.36-48.79
	4	57.22	2.61	56.64-58.36
	5	55.20	2.52	54.65-56.30
	6	49.04	2.24	48.55-50.02
	7	52.74	2.41	52.21-53.79
	8	70.80	3.23	70.09-72.21

Fig. 14. Structure with visible multilayer zone of PP/MMT 1 performed under condition of N-CIM equal to Tm/St/Sn 280/3/12; cross section was chosen from the middle part of specimen.

Contribution of multilayered zones increases, while contribution of MMT increases to 3 and 5 wt%. Accordingly to increment of stroke numbers and time for both melt temperatures (Table 9, Figs. 15, 16). Most developed structure was reported for PP/MMT 3 processed with all maximu values of 3 changeable parameters (Fig. 16).

Table 9.
Flexural strength of PP/MMT 3 [MPa]

Process	Set	Statistical values		
		Arithmetic average σ_{max} [MPa]	Standard deviation	Confidence interval min-max
CIM	1	59.32	2.71	58.73-60.51
	2	75.89	3.46	75.13-77.40
N-CIM	1	67.39	3.07	66.71-68.73
	2	72.12	3.29	71.40-73.56
	3	92.00	4.20	91.08-93.84
	4	119.27	5.44	118.01-121.65
N-CIM	5	91.00	4.15	90.00-92.82
	6	95.00	4.33	94.05-96.92
	7	107.00	4.88	105.95-109.14
	8	125.00	5.70	123.74-127.50

Fig. 15. Structure with visible multilayer zone of PP/MMT 3 performed under condition of N-CIM equal to Tm/St/Sn 240/3/12; cross section was chosen from the middle part of specimen.
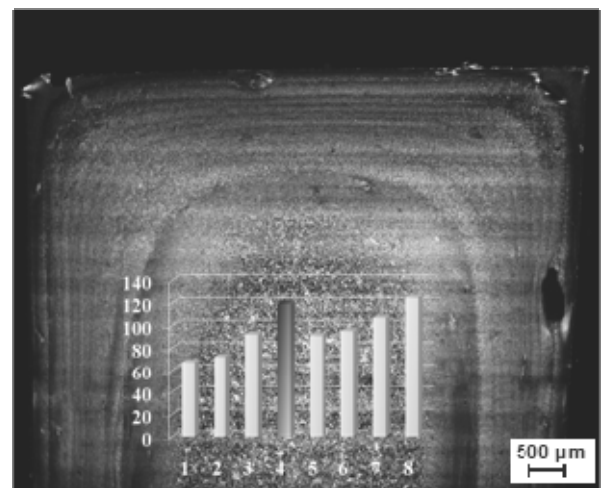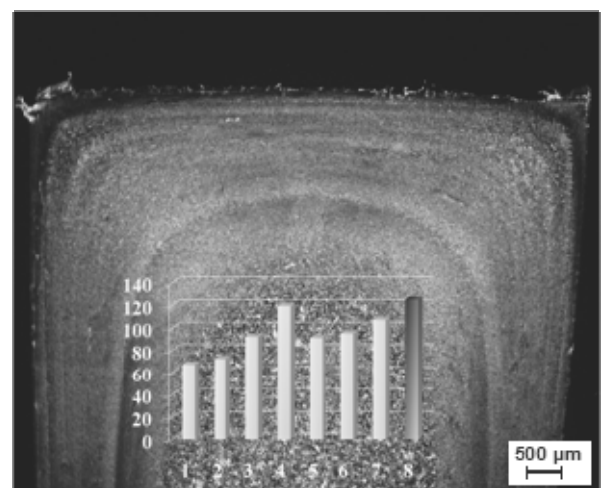

Fig. 16. Structure with visible multilayer zone of PP/MMT 3 performed under condition of N-CIM equal to Tm/St/Sn 280/3/12; cross section was chosen from the middle part of specimen

Table 10.
Flexural strength of PP/MMT 5 [MPa]

Process	Set	Statistical values		
		Arithmetic average σ_{max} [MPa]	Standard deviation	Confidence interval min-max
CIM	1	62.53	2.85	61.90-63.78
	2	81.64	3.72	80.82-83.27
N-CIM	1	60.26	2.75	59.66-61.46
	2	92.74	4.23	91.81-94.59
	3	93.50	4.26	92.57-95.37
	4	111.07	5.07	109.9-113.2
	5	88.81	4.05	87.92-90.58
	6	90.00	4.10	89.10-91.80
	7	104.00	4.74	102.91-106.00
	8	114.00	5.20	112.8-116.2

For specimens with 5 wt% of MMT three sets influenced the structure and reinforced it. Structure was obtained under condition 240/3/12 and 280/3/12 (Table 10, Figs. 17, 19), but also for 280/1/12 (Fig. 18). There is common trend in structure development and can be observable that all highest outcomes of flexural strength were obtained when setting of stroke time and stroke number was at maximum level. That was also predictable that melt polymer subjected to shearing and creating maximum number of layers in multilayer zone will reinforce structure maximally, however verification and setting of limits was necessary. There are also some settings suitable for shattering of MMT agglomerates and as in the case of PP/MMT 5 structure was reinforced also with settings 280/1/12.

Further, double increment of MMT contribution, that means 10 wt%, weaken fully saturated material by MMT. Particles couldn't reach uniform intercalation and micro agglomerates, located in the matrix and subjected to bending, break easily.
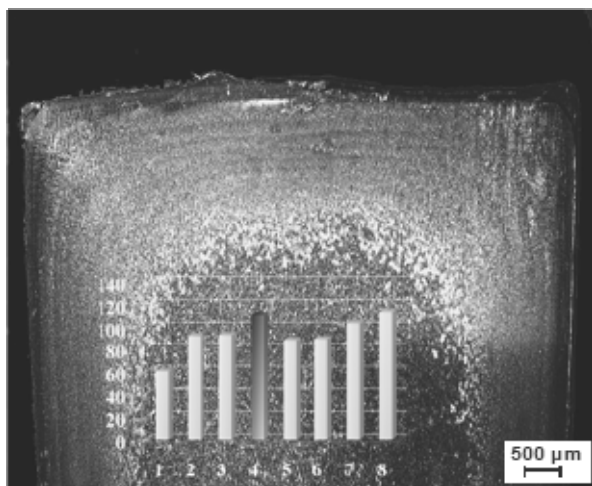

Fig. 17. Structure with visible multilayer zone of PP/MMT 5 performed under condition of N-CIM equal to Tm/St/Sn 240/3/12; cross section was chosen from the middle part of specimen

Fig. 18. Structure with visible multilayer zone of PP/MMT 5 performed under condition of N-CIM equal to Tm/St/Sn 280/1/12; cross section was chosen from the middle part of specimen

Fig. 19. Structure with visible multilayer zone of PP/MMT 5 performed under condition of N-CIM equal to Tm/St/Sn 280/3/12; cross section was chosen from the middle part of specimen
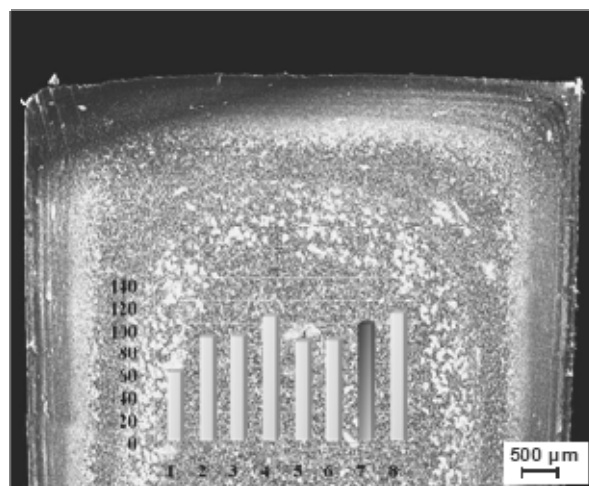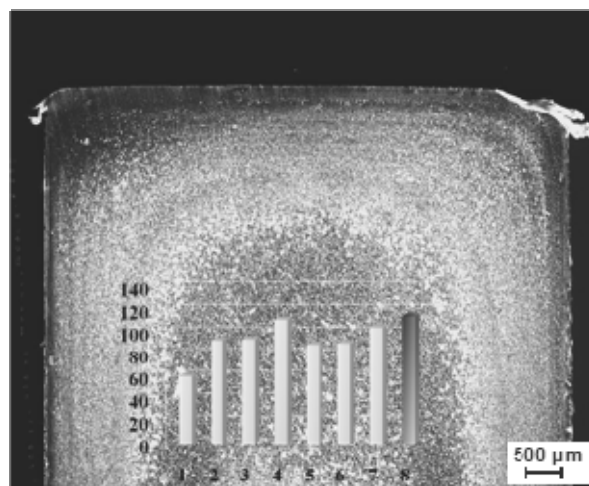
Table 11.
Flexural strength of PP/MMT 10 [MPa]

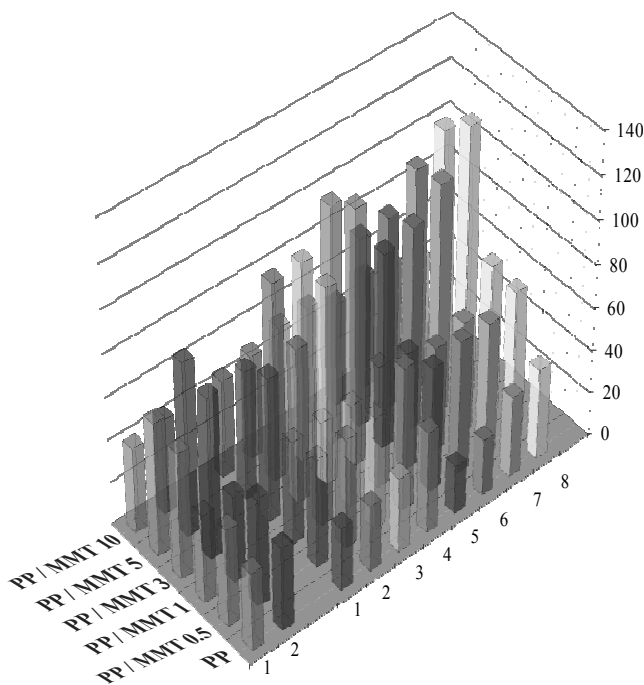| Process	Set	Statistical values		
		Arithmetic average σ_{max} [MPa]	Standard deviation	Confidence interval min-max
CIM	1	40.27	1.84	39.86-41.07
	2	44.66	2.04	44.21-45.55
N-CIM	1	45.77	2.09	45.32-46.69
	2	49.04	2.24	48.55-50.02
	3	54.00	2.46	53.46-55.08
	4	54.72	2.50	54.17-55.81
	5	48.36	2.21	47.87-49.32
	6	53.04	2.42	52.51-54.10
	7	51.00	2.33	50.49-52.02
	8	45.89	2.09	45.43-46.81

Fig. 20. Results of flexural strength (MPa) for nanocomposites and PP accordingly to 2 sets of conventional technique and 8 sets of non-conventional one

4. Conclusions

The platelet reinforcement in the form of MMT nanoparticles and technological solution how to improve properties by reinforcement the structure through control of creation the multilayer zone by use of N-CIM technique satisfied research and brought excellent results.

Multiplication of the shearing, which exists in injection moulding, by application N-CIM technique, creates gradient structure. Induced shearing supports splitting of agglomerations, improve dispersion and intercalation of MMT. Better distribution improves significantly the strength.

Expectations of most interesting results were concentrated close to 3 wt% of nano filling, according to literature and supplier recommendations. Nevertheless not for all mechanical properties this amount of nano clay was the best reinforcement.

The lowest value belongs to pure PP without reinforcement. There is increment for second nanocomposite with 0.5% MMT. Addition of just 0.5% of MMT more insignificantly reduced strength. Further filling of 3% of MMT improved drastically up to 5%. Next nanocomposite confirms that 10% is the final limit for enhancing properties, which are still better that pure based material (Fig. 20).

Comparing to strength, where definitely 5% of MMT was the best enhancement, good stiffness can be obtained at low level of nano contribution.

Addition of nanoparticles improved strength of composites and thanks to linking materials' modification with processing technology in effect has been obtained almost double enhancement of compositions, satisfying initial assumption of this work. DOE schedule was helpful in assigning best and optimized design of average response values and also in 1imizing effects of variability on process assuring robust design.

Nanocomposites significantly react on N-CIM technique providing to well reinforcement of structure and to multilayer zone, as it was reported in previous works.

Nanocomposites processed at higher temperatures showed more stabilized and uniform behaviour regardless on processing set-up. Higher temperature allows for better distribution of nanoparticles, while lower temperature may affect breakage of nanoclay agglomerations due to lower viscosity and stronger shears.

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