

Non-conventionally obtained polymer nanocomposites with different nano-clay ratios

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Received 15.09.2008; published in revised form 01.12.2008

Materials

ABSTRACT

Purpose: Aim of work has been concentrated on investigation of nanocomposites, as promising engineering materials, basing on polymers and organo-modified silicates as nano fillers.

Design/methodology/approach: Conventional injection molding process additionally equipped with external computer controlled manipulation system for inducing the shear rates.

Findings: Evidently reinforced structures at 3 and 5 wt % of nano-clay content inside polymer matrix for different processing settings related to higher shearing time.

Research limitations/implications: Application of nano platelet together with developed injection molding technique brought satisfying mechanical results and development of morphology in the shape of gradient composition.

Practical implications: Reinforced nanocomposites are promising materials with high strength and stiffness and with low cost of raw materials (97 wt% of polypropylene and 3 wt% of 2:1 phyllosilicate).

Originality/value: Wide application of polymer nanocomposites as materials with ameliorates properties render them high potential materials.

Keywords: Nanocomposites; Injection molding; Non-conventional injection molding; Silicates; Polymer processing; Engineering polymers

1. Introduction

Structures of injected polymers obtained under different processing depends on characteristic parameters like heating-cooling rates or flow rate. Investigation of material behaviour at this field has been described in many publications [1-3]. Static crystallization brings spherulite structure and structure modification appears during change of processing temperatures or material deformation i.e. stressing before or during crystallization [4, 5].

Modification of solidifying structure brings gradiently arranged morphology [6-8].

Injection molding as technique worldwide used for applications with very wide field, produced also in multicavity moulds, starting at domestic products and reaching out advanced engineering composites has been used in the research [9,10]. Solidifying melt moved inside cavity reciprocally creates developed structure with skin-core zones, as in the conventional injection molding, and mean highly oriented zone. Gradient shear zone is obtained. Crystallizing and solidifying molten polymer is

undergo to high shear rates and number of layers depends on processing condition. Morphology then depends on moulding processing setup and polymer properties as well [11, 12]. Molten polymer is subjected to shear and elongational flow, prior to crystallization. Closer to frozen layer at mold side shear rate dramatically increases and formation of extended particles is reported [13, 14] accordingly to the profile of shear rate and melt flow model [15]. The challenging area is reinforcing polymer composites by compounding nanofillers with polymer matrix e.g. iPP (Table 1) by melt mixing through extruding and further forming or injection molding by direct forming desired shape. There are many possibilities of forming nanocomposites, but the main goal for all techniques is good exfoliation of particles and in effect improvement of mechanical properties. Fragmentation of agglomerated particles and well distribution can be obtained by inducing high shear into processing. This element of production is satisfied by SCORIM process, where in the shear zone and especially on the layers' boundaries exists high shear rates additionally intensified by transportation of melt flow front along quasi-frozen layer. More details will be discussed in further work. In this article work is focused on mechanical behavior of nano-reinforced polymer composites subjected to high shear rates by SCORIM technique.

Table 1. List of abbreviations used in article

Material	
iPP	Isotactic Polypropylene type Moplen HP501M - matrix
MMT	Montmorillonite type Nanofil5 (distearyl-dimethyl-ammonium ion exchanged bentonite) - nanoclay
Technology	
LCP	Liquid Crystal Polymer
CIM	Conventional Injection Moulding
N-CIM	Non-conventional IM
SCORIM	Shear Controlled Orientation in IM
Experiment	
DOE	Design of experiment
ST	Stroke time
SN	Stroke number
Tm	Melt temperature

2. Experimental procedure

Basic on 3-factorial, 2-level DOE schedule specimens were prepared in quantity of 5 for each experiment in aim to exclude extreme values to possess at least 3 outcomes for mean value. Specimens were tested by 3-point bending test with crosshead speed 10 mm/min (according to the ASTM E399 standard) at controlled room temperature (23°C). 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.

Materials used to the experiment were polypropylene (iPP) and montmorillonite (MMT) (Table 1) at different ratios (Fig. 1).

Three processing parameters were mainly affecting morphology and in effect properties, so why these parameters have been considered as variable (Table 2).

All other parameters included in the molding programme, namely velocity of injection, hydraulic pressure, cooling time (equal to stage time of mode C) were kept constant. CIM technique has just one variable parameter – the melt temperature. Cooling time and melt temperature was equal for both techniques.

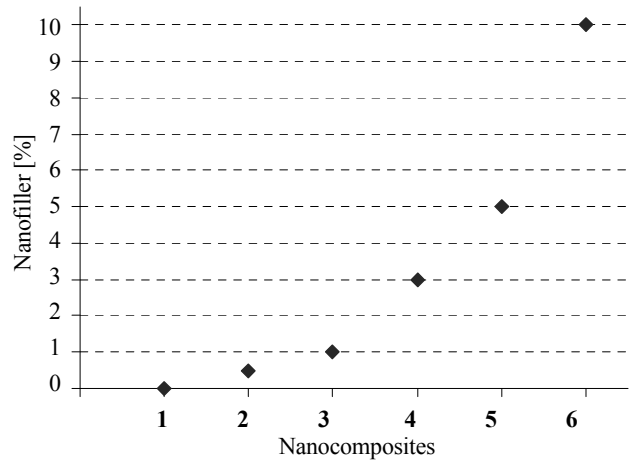


Fig. 1. Quantity of nanofiller in polymer matrix

Table 2. Set of variable and constant parameters for processing of gradient polymer nanocomposites by N-CIM technique

N-CIM			
		Varied parameters	
Mode A		min	max
(reciprocation)	Stroke time [s]	1	3
	Stroke number	3	12
Mode C		Constant parameter	
(holding)	Cooling time [s]	30	

Depending of these variable parameters time of shearing has been considered and included in the experimental plan for different runs (Table 3), symmetrically divided into two temperature levels, lower 240°C and higher 280°C. Nextly ST and multiplication of it by SN was summarized. Run 1 and 4 then are the representations of CIM techniques, where ST and SN are not taken into consideration. Run 2 and 5 for temperature 240°C and 280°C adequately, are the lowest values of ST (1s) and SN (3 strokes), what gives total shearing time of 3s. Highest values of variable parameters are the runs 3 and 6, where is reported maximum of shearing time (ST equal to 3s and SN equal to 12 strokes). Time of injection (1s) was added to each run as the time of initial shearing.

Specimens, injected by N-CIM technique, present different results upon filling by MMT and settings of processing. Variable parameters (ST, SN and Tm) and their mutual rearrangement.

Table 3.
Set of parameters for 6-run schedule

Processing set-up		
Run	Tm [°C]	Time of shear [s]
1	240	1
2	240	4
3	240	37
4	280	1
5	280	4
6	280	37

Pure PP and each of 5 nanocomposites was then prepared according to 6 runs' settings giving totally 36 outcomes as complementary information of processing influence on reinforcement and for further statistical analyzing.

3. Discussion of experimental results

Time of shear included in the experiment is correlated with SCORIM system. Movements of pistons, which are responsible for transferring reciprocally melt polymer, are based on 2 levels – lower and higher. Accordingly to table 1, ST has two values – 1 and 12 seconds - the real time of moving piston. During this time flow front moves along cavity inside mold creating the layer. Set-up is then symmetrically prepared for two extreme temperatures (240 and 280°C). For each temperature 2 extreme values of ST (1 and 3) and SN (3 and 36) has been set. Additionally 1 second of injection time was added to each process.

Aim of investigation was directed to obtain reinforced structure through enrichment by nano particles and by technique as well. Highly oriented layers created during second phase of injection process, while SCORIM works, exhibit good dispersion and particles are subjected to strong tension. This phenomenon, mentioned in literature by D. Rosato, considered fact, that particles located closer to skin are extended due to faster cooling and simultaneously strong shearing (Fig. 2). The same effect can be achieved in SCORIM system and multiplied, because repeating sequences of reciprocating movements tailor structure developing shear zone and inducing shape modification of particles. To approve that phenomenon firstly was prepared experiment with PP/LCP composite in ration 70/30 wt% respectively. Micro-sized particles are suitable to observe their shaping after processing. The goal of experiment has been successfully reached and particles of LCP closer to skin stretched due to subjected forces (Fig. 3).

This lamellae-like reinforcement was generated by application of technique at 280°C and with 12 strokes (maximum number in all experiments). Total shearing time was 13 seconds. Following this direction set-up was prepared for nano reinforced polymers. In DOE lowest level of ST (1s) was combined with lowest level of SN (3) and inversely, high ST (3s) with high SN (12). In effect two extremes of SCORIM parameters (4s and 37s of shearing time) was investigated at two extreme temperatures to get marginal overview of mechanical response.

Expectations of most interesting results was concentrated close to 3 wt% of nano filling, according to literature and supplier recommendations[16-18]. Nevertheless not for all mechanical properties this amount of nano clay was the best reinforcement.

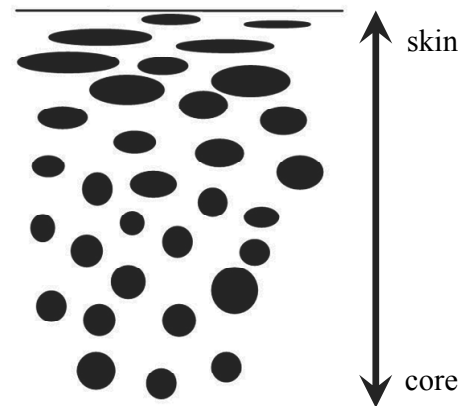


Fig. 2. Influence of shear during injection on the shape of particles across the specimen; top line – skin [13]

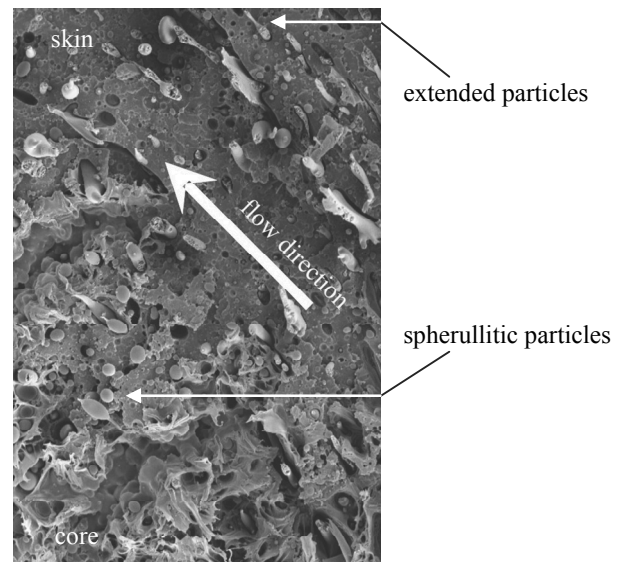


Fig. 3. Differences between particles from core and skin regions, subjected to different shear rates; sequence of Tm-ST-SN was 280-1-12

Extended particles clearly presented on scanning electron microscopy micrograph above (Fig. 3) was promising path for further experimental work. Obtained results of nanocomposites' testing approved about this rightness satisfying intended goals.

High shear rate during injection molding modified micro sized particles. Multiplication of this shearing effect by application SCORIM technique, which creates gradient structure, affect shape of particles in wider shearing zone. Nevertheless induced shearing doesn't affect shape of nano particles, but it supports in exfoliation and splitting of agglomerations. Better distribution improve significantly the strength. Combination of simultaneous use of N-CIM technique and nanoparticles has been approved by satisfying results. Highest energy at break was reported for 3 and 5% of MMT (Fig. 4) with slight difference summarizing all runs. These two nanocomposites show good results not for all runs. As can be observed the third and fifth run reinforced structure mostly.

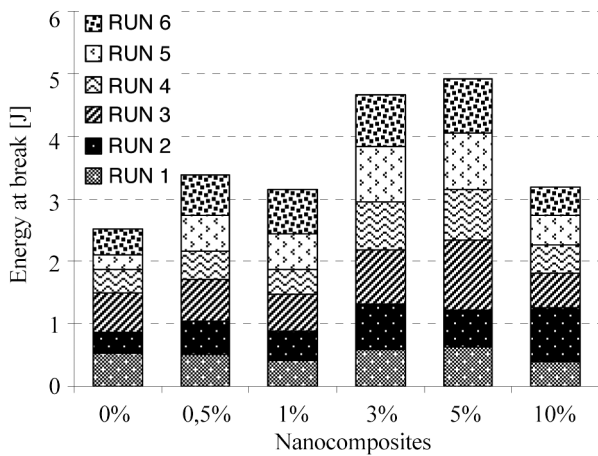
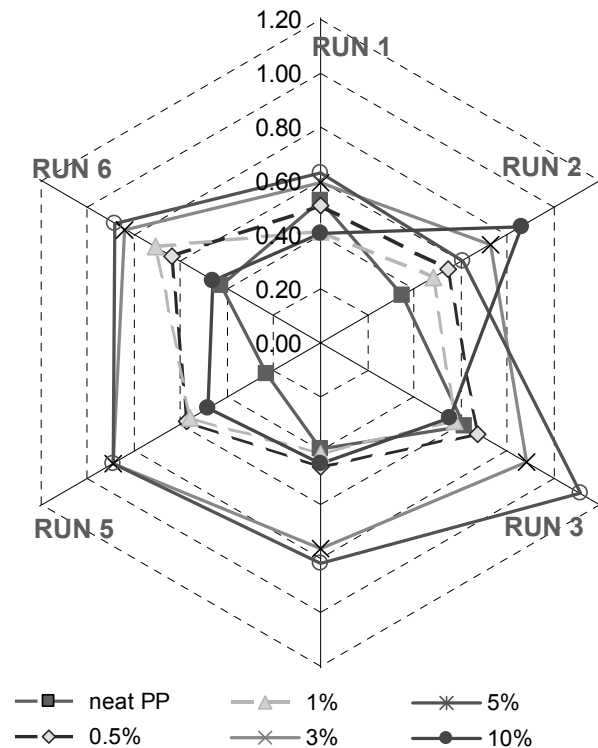


Fig. 4. Energy at break for 36 conditions of processed nanocomposites (6 runs for 6 compositions each)



Energy at break [J] for all nanocomposites' conditions

Fig. 5. Flexural Modulus for 36 conditions of processed nanocomposites (6 runs for 6 compositions each)

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 than pure based material.

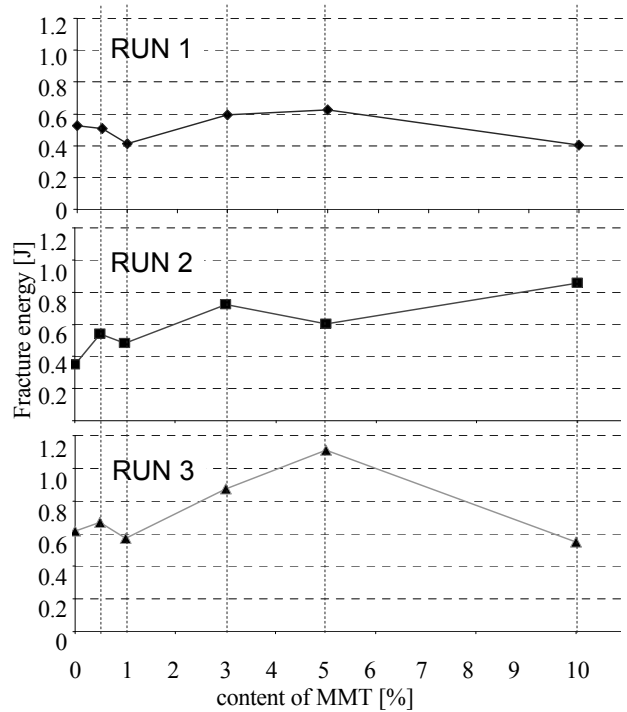


Fig. 6. Fracture energy for 1, 2 and 3 run for all nanocomposites with different MMT content

Distribution of nano galleries is impeded by agglomerations, which still exists in the structure and may abate working as stress concentrators. More focused overview considering run by run is presented on Figure 5. For the sixth nanocomposite (according to Fig. 1) run was the mostly significant doubly higher than other runs. For the pure PP run 1 and 3 gave best results, both at 240°C for simple injection (no SCORIM) and for maximum of runs.

The best value of pure PP still defines almost half value of the best MMT nanocomposite.

Following the change of fracture energy across all nanocomposites (Fig. 6) can be visibly reported that just run 1 weakens after filling matrix by nano particles.

All other runs, especially the third and fifth one, increase value of fracture energy. Run 3 rises after addition of 3% MMT and continues rising up to 5%. After that grammatically fall down even lower than initial value. Runs 4, 5 and 6 (Fig. 7) are stabilized after 1% of MMT, presenting similar values for 3 and 5% and as in the case of almost all cases drops at 10%.

Flexural Modulus doesn't represent huge divergence in results including all runs (Fig. 8).

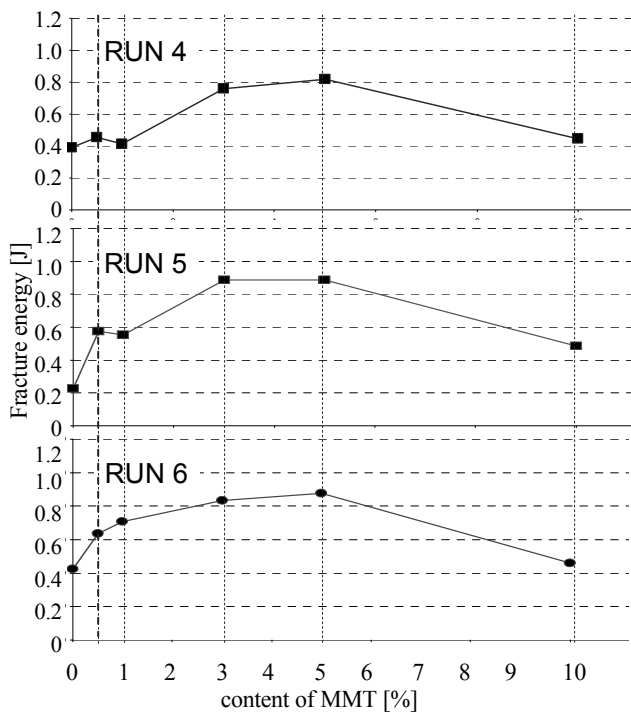


Fig. 7. Fracture energy for 4, 5 and 6 run for all nanocomposites with different MMT content

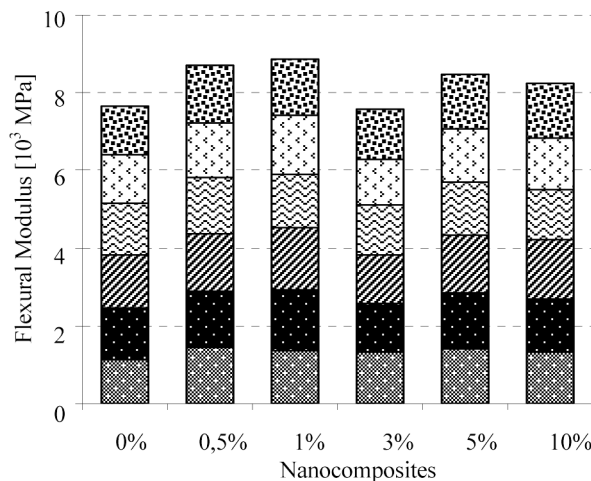
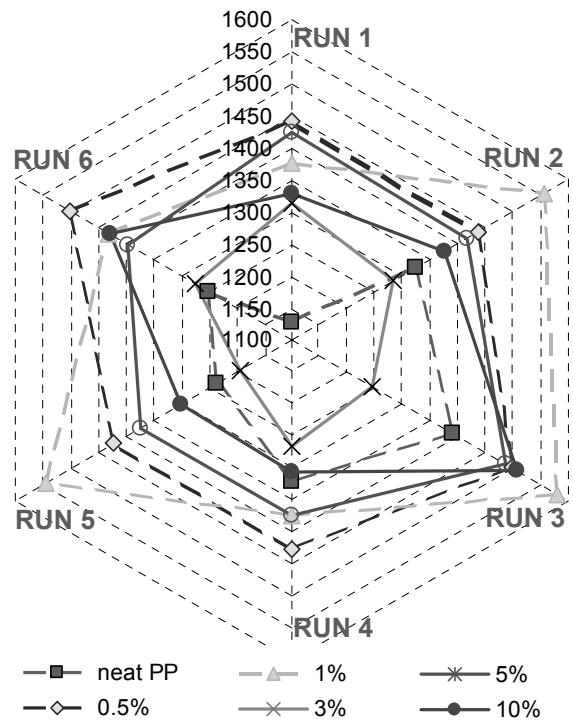


Fig. 8. Flexural Modulus for 36 conditions of processed nanocomposites (6 runs for 6 compositions each)

For each nanocomposite results are high. Inversely to energy at break the fourth nanocomposite has lowest values. More precisely can be observed behaviour of particulate runs at Fig. 9. Significant here is run 3 (ST and SN are maximal) for 1 and 10% of MMT. Similarly, as in the case of energy, pure PP has lowest stiffness. Interestingly second nanocomposite (with just 0.5% of MMT) represents high results for all runs.



Flexural Modulus for all nanocomposites' conditions

Fig. 9. Flexural Modulus for 36 conditions of processed nanocomposites (6 runs for 6 compositions each)

4. Summary

Total overview of different nanocomposites processed in many diversified ways with CIM and developed injection molding technique, brought complex report of their behaviour. Within this data, which contains totally 36 findings for both flexural and fracture tests, can be easily extracted best results of all experiments.

Comparing to strength, where definitely 5% of MMT was the best enhancement, good stiffness can be obtained at low level of nano enrichment. Comparing to previously mentioned fifth nanocomposite, mostly strengthened, the second and third nanocomposites realize the same criterions and are stiffest.

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 minimizing 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 [7, 14].

CIM technique, represented by run 1, is weaker than reinforced runs reaching maximum at 0.6 J, what was expected. Obtained reinforcement was surprisingly high reaching 1.1 J in the case of 3rd run for 5% what determines 90% of increment.

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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