Development of microstructure affected by in-mould manipulation in polymer composites and nanocomposites

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Manufacturing and processing

ABSTRACT

Purpose: Investigation of microstructure of polymer nanocomposites subjected to high shear rates during solidification phase.

Design/methodology/approach: Injection moulding technique combined with specially designed mould gives possibility to manipulate solidifying polymer or polymer's mixture inside cavity mould.

Findings: Significant increment of fracture energy depending of applied conditions including melt temperature and time of shearing of polymer blend.

Research limitations/implications: Obtained nanocomposites contain better mechanical properties comparing to polymer composites and application of SCORIM technique brought satisfying and improved results comparing to conventional methods.

Practical implications: Implicated advanced technique to conventional injection moulding gives high performance material with good increased toughness and nanoplatteled particles, uniformly distributed, thanks to the applied technique, inside matrix well reinforce final products.

Originality/value: SCORIM technique is rarely used technology and has influence on creation and development of morphology of processed materials.

Keywords: Nanocomposites; Engineering polymers; Polymer processing; Injection moulding; SCORIM

1. Introduction

Commodity thermoplastics, as polyolefins PP or PE (Table 1), are commercially available and applicable materials. Blending polyolefins with engineering plastics, as PC, ABS [1], or nanofiller [2] improves the mechanical properties of polymeric materials. The incorporation of the fillers into polymer matrices is an effective technique to improve or modify some properties of neat polymers and as it was reported by M. Arroyo [3] highest influence on final properties have particles with a high shape factor (length/diameter ratio) such as fibres or laminate fillers.

The possibility of improving mechanical properties such as toughness and stiffness as a function of interfacial coupling and processing conditions has been investigated [4]. It confirms importance of application of nanocomposites materials in which the reinforcing elements are nanoplatelet fillers distributed anisotropically inside isotropic polymer matrix. Expected improvement of properties can be achieved by the selection of the composite components (matrix and reinforcing phase), their blend

ratios and distribution of the dispersed phase, which can be obtained during blending and thermomechanical treatments [5, 6], Fakirov and co-workers reported, that upon cold or hot drawing and annealing of the drawn blend structure is oriented and microfibrils are formed in the minor phase. Further development of the structure was obtained by subsequent heat-treatment [7]. Molten polymers are subjected to various kinds of flows during processing such as extrusion or injection molding 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 [8-10]. Baranov and Prut reported on the high modulus of isotactic polypropylene (iPP) produced by drawing in to stages, which exhibited a Young's modulus of 30-35 GPa. The increase in the mechanical properties is mainly influenced by the reduction of segmental mobility of molecular chains in the inner spherulite amorphous regions of a polymer [11]. Extruded products like after injection-molding exhibit a skin-core morphology [12-14]. Development of structure can be obtained by combining several mechanisms [15] as drawing of the blend and influencing crystallization by high shear rate. It can be accomplished by SCORIM technique under various processing set-up [12, 16, 17].

Additionally together with advanced technique use of nanoscaled clay affects final morphology. Many of clay are aluminosilicates with a layered structure divided on tetrahedral sheets of silica $SiO4^{4+}$ bonded to octahedral sheets of alumina $AlO6^{9-}$ [18]. Montmorillonite as common smectite clay contains arrangement of these sheets in proportion 2:1 ratio of silica to alumina (Fig. 1).

It is well known that a beautiful superstructure of polymer crystals can be created by crystallization during flow [20]. Specific is also fact that in crystalline structure of polyolefins, subjected to stress (like during injection moulding process) appears shish kebab structure, firstly described by Penning [21]. In his work he presents a model of developed structure, where extended chain crystals are surrounded by folded chain crystals called shish and kebab respectively (Fig. 2). Firstly is formed long fibrelike core (shish) during a crystallization process and under stress. Then platelike lammlar crystals (kebabs) overgrow this shish structure epitaxially. Although this shish-kebab structure was observed in the 1960s, the formation mechanism of shish-kebab

structure is still actual subject in research [22]. The longest chains are mainly responsible for shish-kebab morphology construction, accordingly to the coil-stretch transition theory, which explain that due to deformation of polymer melt, consisting entangled chains of different, the chain segments aligned with the flow direction can be subjected to the coil-stretch transition. The rest of segments stays in the coiled state. Oriented high molecular weight species play a prominent role in formation of the stretched zones, where shish originates [23, 24] and when crystallization of oriented long chains forms the shish cores, consecutively short chains crystallize from the lateral side of long-chain crystals creating kebabs [25].

Injection moulding as technique for obtaining such structures and commonly used technique for wide range of applications with domestic and engineering purpose has been used in the research. Solidifying melt manipulated inside cavity mold creates developed structure with skin-core zones, as in the conventional injection moulding, and highly oriented shear zone. Gradient shear zone is obtained by reciprocal flow movements inside the mould cavity due to extracting and retracting of hydraulic pistons of SCORIM mould (Fig. 3). Solidifying molten polymer is undergo to high shear rates and number of layers depends on processing condition.
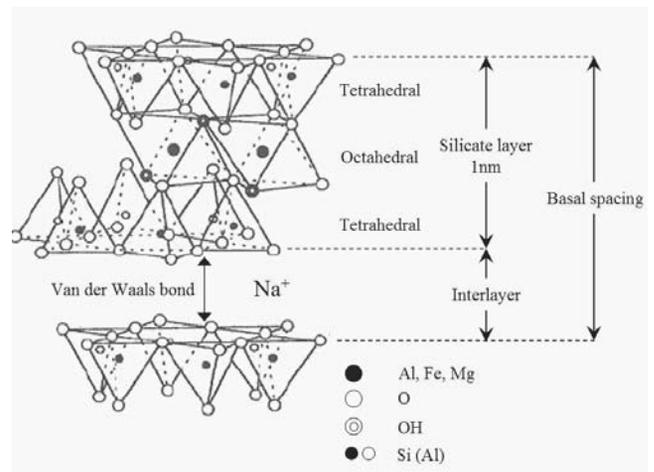
Fig. 1. Schematic illustration of atoms arrangements in a typical MMT layer [19]
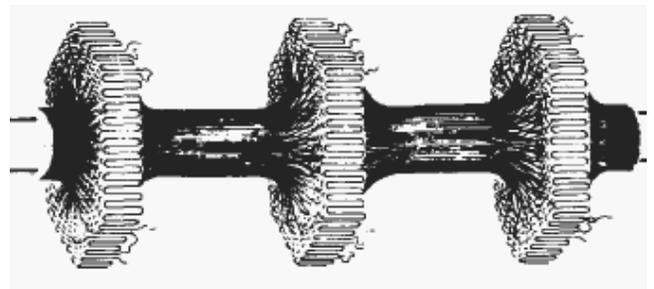
Fig. 2. Models for polyethylene shish-kebabs with different distributions of interlamellar fibrils [21]

Table 1.
Abbreviations used in article

Abbreviations	
Material	
Polypropylene - *matrix*	PP
Montmorillonite – *nanoclay, reinforcement*	MMT
Processing	
Specific setting of Tm-ST-SN parameters	Run
Conventional Injection Moulding	CIM
Non-conventional IM	N-CIM
Shear Controlled Orientation in IM	SCORIM
Melt temperature	T_m
Stroke time	ST
Stroke number	SN
Testing	
Design Of Experiment	DOE
Polarized Light Microscopy	PLM
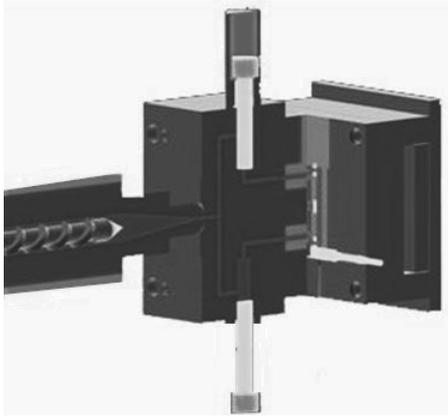
Fig. 3. SCORIM mould with two external pistons responsible for creation of multilayer structure [26]

2. Materials and methods

In the experiment polypropylene (PP) as matrix material has been used and montmorillonite (MMT) as reinforcing phase was added to the particular compositions (Table 2).

Four composites with variable ratios of materials and neat PP for comparison purpose was chosen to experiment. Specification of materials are listed below:

- Polypropylene from Basell, type Moplen HP 501M, with density of 0.9 g/m^3
- Montmorillonite from Nanofil 5, Süd-Chemie, with density of 1.8 g/m^3

Experimental plan has been set by using Taguchi orthogonal array accordingly to DOE. Processing setting were adjusted for both injection moulding techniques conventional and non-conventional (Table 3).

CIM contains just 1 variable parameter, namely melt temperature. In this case total shearing time (last column in the Table) is equal to injection time, where shearing is also reported and oriented skin is obtained.

Table 2.
List of investigated composites arranged by wt% of particular components

	Abbr.	PP	MMT
1	Neat PP	100	-
2	PP/MMT 0.5	99.5	0.5
3	PP/MMT 5	95	5

Table 3.
CIM variable processing parameters

Run	Melt temperature (T_m) [ºC]	Stroke time (ST) [s]	Stroke number (SN)	Total shearing time [s]
		SCORIM parameters		
1	240	-	-	1
2	280	-	-	1

N-CIM programme contains 3 variable parameters – one of them is the melt temperature as in the CIM and 2 others are related with SCORIM mould, responsible for time and number of piston movements (ST and SN respectively). Four different conditions were compared considering minimum and maximum of shearing time. Increment of shearing time was also related with an extension of stroke time and number of strokes. Melt undergo to bigger number of strokes gave more developed morphology with increased amount of layers. Parameter called stroke time represents time between particular movements. Extending of time was aimed to give time distance between creation consecutive layers during solidification phase. However specific conditions called further as runs brought satisfying results, not always improving mechanical properties due to increasing of parameter values. Table 4 lists settings for changeable parameters exploited for producing composites.

Table 4.
N-CIM variable processing parameters

Run	Melt temperature (T_m) [ºC]	Stroke time (ST) [s]	Stroke number (SN)	Total shearing time [s]
		SCORIM parameters		
3	240	3	12	37
4	280	3	12	37

Totally were compared 20 conditions – four particular settings for each of five compositions. For all specimens in both conditions hydraulic pressure has been 150 bar and kept constant, as well as other parameters - holding pressure (50 bar), mold temperature (30ºC), cooling time (30 s), injection flow rate (15 mm/s).

Temperature settings of five barrel zones of the injection unit in moulding machine for 2 temperature levels is presented on Fig. 4 below.
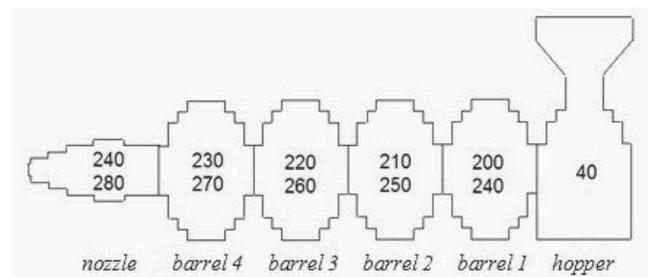
Fig. 4. Temperature profile of injection unit for minimum and maximum schedule

Morphology of blends has been observed microscopically in polarized light on Olympus Light Microscopy type BH2 with additional digital camera Olympus DP11. PLM was suitable technique to detect layers. Counting and measuring has been achieved by computer-aided analyzing programs Quantimet 500C and LeicaQWin. 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 surface quality for observation was achieved.

To execute mechanical testing Instron universal testing machine type 4505 was used. Speciens were prepared accordingly to the norm ASTM E399 for 3-point bending fracture test with crosshead speed 10mm/min and with notch depth of 6.35 mm by using notch cutter CEAST type 6816 with the blade type 6530. Ate the end notch was sharpened by razor blade. Tests were performed at stabilized air condition – 50% of humidity at 23ºC.

3. Results and discussion

Visible difference between CIM and N-CIM morphology is the shrinkage (Fig. 5) of CIM specimens (17%). Avoiding this shrinkage was achieved, when N-CIM technique was used undergo out-of-phase mode, where alternating extension and retraction of the melt in the mould cavity filled-up tightly cavity. For this conditions big core occupies 90% of specimen and outer morphology consists on one external layer – skin, typical for CIM. Core is then 10 times bigger than shear zone. Neat PP evidences structure development and complete rectangular shape achieving after use of N-CIM technique. Core occupies less area, while shear zone appears reinforcing structure (Fig. 6), where slightly increases fracture toughness after increasing shearing time. Better shearing effect and improvement of mechanical properties is reported for lower temperature, where viscosity and shear rate is higher.

Much more interesting structure was obtained for nanocomposites (Fig. 7). Clearly visible multilayer structure appears occupying about 70% of total area. Lower temperature is most suitable for gradient structure formation due to higher shear rate. It means that comparing to CIM shear zone with outer skin increased triply.

Run 1
CIM/ 240ºC

Run 2
CIM/ 280ºC

Run 3
N-CIM/ 240ºC

Run 4
N-CIM/ 280ºC
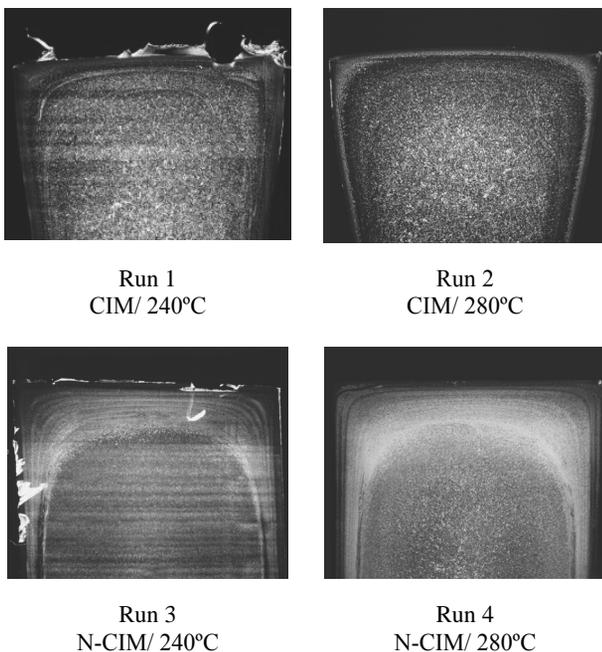
Fig. 5. Light polarized microscope photographs of neat PP for CIM (run 1-2) and N-CIM (run 3-4) conditions
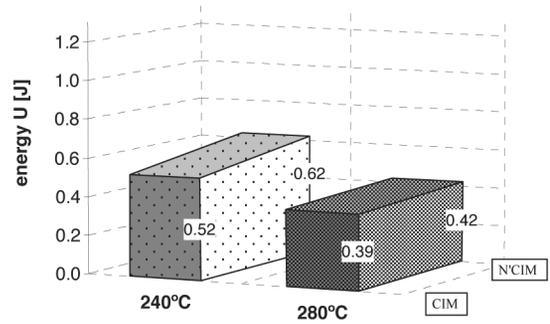
Fig. 6. Fracture energy values for extreme temperatures for neat PP

Run 1
CIM/ 240ºC

Run 2
CIM/ 280ºC

Run 3
N-CIM/ 240ºC

Run 4
N-CIM/ 280ºC
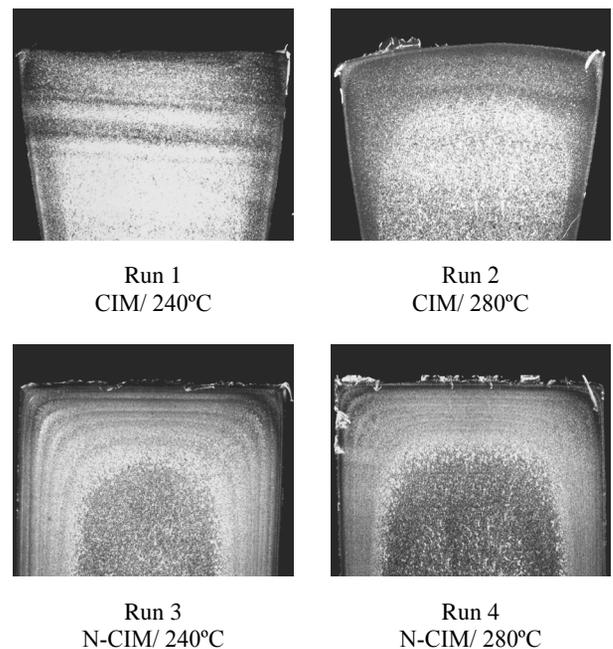
Fig. 7. Light polarized microscope photographs of PP/MMT 0.5 for CIM (run 1-2) and N-CIM (run 3-4) conditions

Addition of 0.5 wt % of nanoplatelet clay to polymer matrix improved toughness for CIM for higher temperature and for both temperatures use of N-CIM technique increased mechanical performance of more than 30% (Fig. 8).

Increment of quantity of nanoclay of 10 times (PP/MMT 5) once more reinforced composite bringing even better results than for PP/MMT 0.5.

CIM technique gives satisfying results for both temperatures, containing best result for run 3. For this run, subjected to low temperature, application of N-CIM technique dramatically improved toughness of 76% (Fig. 10). This structure (Fig. 9, run 3) is highly compacted with multilayer zone (65% of total area) and with spherullitic core (35%).

Higher temperature doesn't present such big difference between techniques, however good results are kept on high level for both CIM and N-CIM technique (Fig. 10).
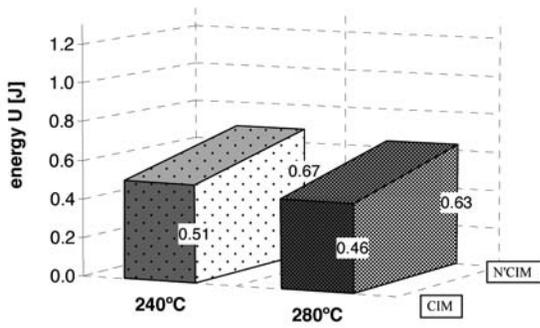
Fig. 8. Fracture energy values for extreme temperatures PP/MMT 0.5 nanocomposite

Run 1
CIM/ 240ºC

Run 2
CIM/ 280ºC

Run 3
N-CIM/ 240ºC

Run 4
N-CIM/ 280ºC
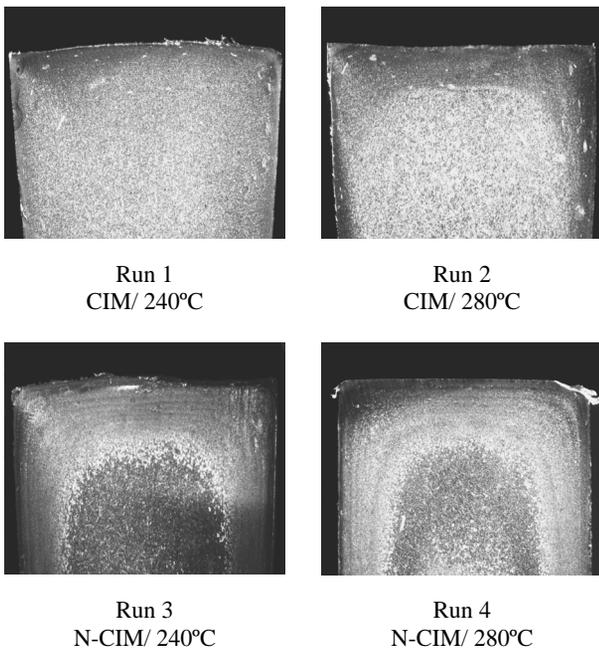
Fig. 9. Light polarized microscope photographs of PP/MMT 5 for CIM (run 1-2) and N-CIM (run 3-4) conditions
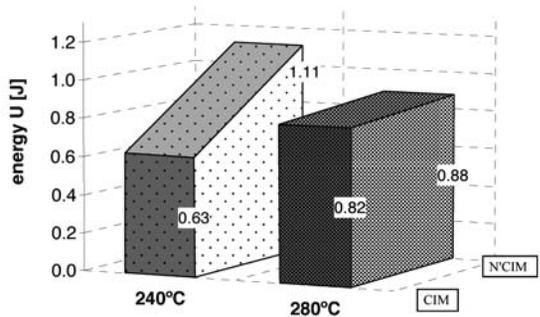
Fig. 10. Fracture energy values for extreme temperatures PP/MMT 5 nanocomposite

Polymer nanocomposites are promising engineering materials with good mechanical results and highly developed structure. This structure could be obtained just by using advanced technique of injection moulding, mentioned in this paper. Overall view of nanosized particles on morphology (Figs. 11 and 12) confirms their affection on toughness, which increases together with its increment. For all conditions increment of MMT improved mechanical performance. Best improvement was reported for lower temperature and N-CIM technique reaching 1.11 J and lowest value of 0.39 J, which is quasi 3 times less (284%), for extreme condition, namely for higher temperature and CIM technique. This is evident proof for rightness in application of SCORIM technique to polymer nanocomposites.
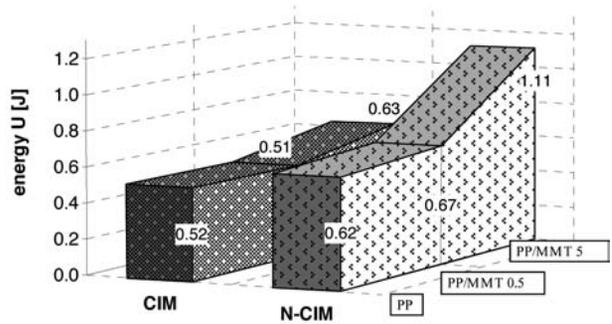
Fig. 11. Fracture energy values at 240ºC for both techniques in the function of increment of nano particles
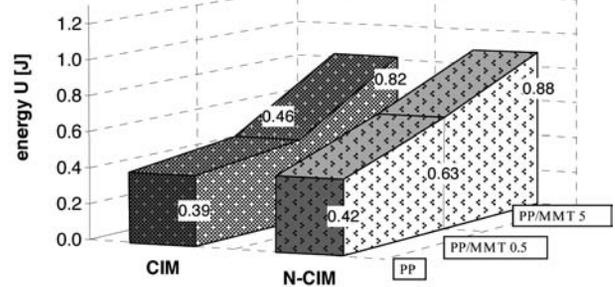
Fig. 12. Fracture energy values at 280ºC for both techniques in the function of increment of nano particles

Mentioned shish-kebab structure and its evidence will be further investigated in future research. Confirmation in literature of existence shish-kebab structure in the skin zone is promising investigation for SCORIM technique, where not just skin, but much more layers is obtained. It can be also explanation, why even in the case of pure PP increment of toughness is reported (Fig. 6).

It can be expected that low temperature and high shear rate supports in uniform distribution of nano plates inside material, especially in shear zone (as for run 3 of PP/MMT 5). Material subjected to high shear rates, particularly accompanying during solidifying phase, may cause also well exfoliation of clay galleries. This nanoscale influence has powerful reflex on morphology and mechanical reinforcement. Further investigation is obligatory.

Acknowledgements

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