

Morphology diversity and mechanical response of injection moulded polymer nanocomposites and polymer-polymer composites

M. Bilewicz^{a,b*}, J.C. Viana^a, A.M. Cunha^a, L.A. Dobrzański^b

^a IPC - Institute for Polymers and Composites, Department of Polymer Engineering, University of Minho, 4800-058 Guimaraes, Portugal

^b Division of Materials Processing Technology and Computer Techniques in Materials Science, Institute of Engineering Materials and Biomaterials, Silesian University of Technology, ul. Konarskiego 18a, 44-100 Gliwice, Poland

* Corresponding author: E-mail address: billy@dep.uminho.pt

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ABSTRACT

Purpose: This work was performed in the aim of exploring non-conventional injection moulding technique and to study the effect of processing thermomechanical treatment on the morphology and properties of polymer-polymer composites.

Design/methodology/approach: Multilayered highly oriented skin regions induced by high shearing of the melt were obtained during non-conventional injection moulding process. Structure development has been observed in the polarized light microscope and by scanning electron microscopy. The fracture energy has been calculated from notched bar specimens.

Findings: The processing variables (melt temperature, stroke time and number) are determinant of the fracture energy of the neat PP. Higher setting of these processing variables gives enhanced fracture energy (25% higher). Immiscible polymer blend of PP/PC processed by melt manipulation techniques show improved fracture toughness compared to neat PP. Addition of MAP to PP/PC did not affect the fracture energy for low setting of the processing variables, but significantly decreased it for high adjustments. The fracture energy of nanoclay reinforced PP is the double of the neat PP, for both melt temperature settings. Lower values of fracture energy have been obtained for polymer-polymer composite of PP/PC reinforced with nanoparticles (3-fold lower).

Research limitations/implications: Further work contains research of different materials' ratio, as well different polymer-polymer compositions (e.g., PP/PS and PP/LCP). Other mechanical properties will be assessed.

Practical implications: The improvement of mechanical response is sharply apparent by use of SCORIM technique and by the use of nanoparticles reinforcement.

Originality/value: This polymer processing technology is promising route for morphology manipulation and improvement on the mechanical properties of polymer systems. Research studies on processing-structure-properties relationships of polymer-polymer composites and nanocomposites moulded by melt manipulation techniques are scarce.

Keywords: Heat treatment; Polymer-polymer composites; Nanocomposites; Non-conventional injection molding; Structure-properties relationships

1. Introduction

1.1. Diversity of morphologies

Reinforced and self-reinforced polymer-polymer composites are nowadays common potential group of materials for high demanding performance applications. In this group the explored and required properties are obtained mainly by selection of the type of polymeric components, eventual added compatibilizer and their relative ratios. The mechanical and physical properties of these polymer-polymer composites arise not just from the combination of polymer compounds, but also from the morphologies developed (e.g., at the interface and of the matrix). Furthermore, eventual polymer-polymer reactions (e.g., copolymer formation, considering also immiscible polymer blends in which are included most of the polymer combinations) occurring due to the thermomechanical treatment applied during processing (e.g., injection moulding) wide the range of structural control for tailored mechanical performance. The diversity of morphology can be additionally specified by the shape (rod, sphere or plate), size (micro, nano) and distribution of dispersed phase in the matrix [1, 2, 3].

1.2. Non-conventional melt manipulation injection moulding techniques

Despite that properties target can be achieved by manipulation of ratio and type of components, the processing is also fundamental and responsible for the mechanical response of the mouldings. In this context, special non-conventional injection moulding techniques have been developed based on the melt manipulation during the solidification phase. Such processes include Shear Controlled Injection Moulding – SCORIM [4, 5], Push-Pull [6-8] and Vibration Assisted Injection Moulding [9]. The main difference of these non-conventional melt manipulation injection moulding processes in comparison to conventional technique (CIM) is the way the melt is treated during the solidification stage. In CIM, during one cycle, the polymer melt is injected, packed and cooled in the mould cavity. After melt injection there is limited possibility to manipulate the morphology. The non-conventional melt manipulation injection moulding gives possibility to control the highly oriented shear zone in the moulded components that allows enhancing the mechanical properties of polymeric material systems. The moulding of polymer-polymer composites by these techniques is scarcely reported in the literature.

The equipment conformed to non-conventional injection techniques may also base on the CIM machine. In the case of SCORIM, the main difference is in the mould, where the typical fixed mould plate has been replaced by the special unit (Fig. 1) combined with two hydraulic pistons (Fig. 1 and 2). This SCORIM head device (Fig. 3) introduces additional operative variables (such as the stroke time, the stroke pressure, the temperature of the manifold and 3 independent operative modes) enlarging the possibilities of morphology manipulation.

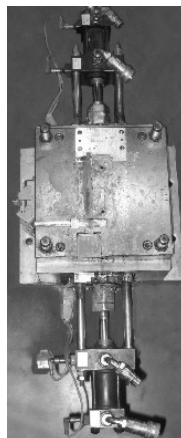


Fig. 1. SCORIM mould plate with two pistons

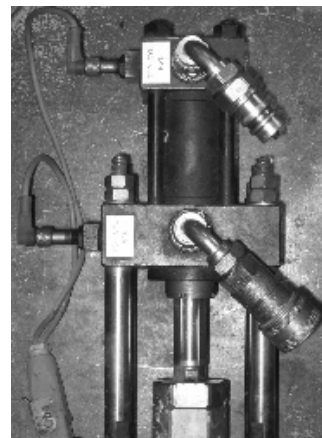


Fig. 2. Top piston of the SCORIM unit

The melt, provided through one hot-runner channels, fills out the cavity from one side through one gate. Once injected melt material fills the cavity the SCORIM stages initiate. One of three modes can be use, referred as mode A, B and C.

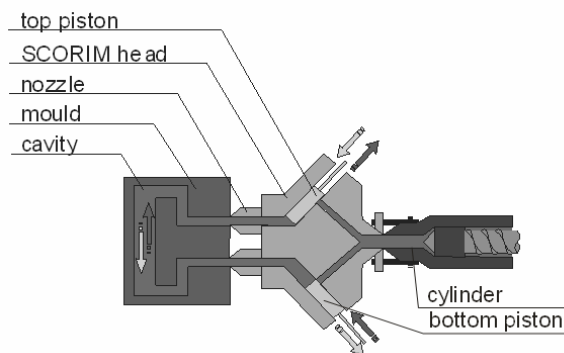


Fig. 3. Scheme of the SCORIM head

Mode A relies on the force and retraction of the molten material by pistons in sequential movements (strokes). Mode B consists on the parallel reciprocation of the pistons with the aim of overpressing the material. The mode C is generally finishing each moulding cycle and both pistons are kept under a static hydrostatic pressure (as in the holding phase in CIM). Combinations of these SCORIM head operative modes can be optionally varied.

While during one movement of the pistons, the melt directed in one direction is getting solidified, next movement initiates the creation of next layer directed parallel with opposed flow direction. As a consequence, the SCORIM mouldings develop a typical microstructure, as a result of the high shear stress fields applied at the solidifying interfaces and treated by actuated external pistons. This microstructure is comprised of external highly oriented multilayers and a spherulitic core. The thickness of these layers, as well their number, depends on the selected process variables setting (e.g., stroke number and time). This

practical application of SCORIM cycle has proved the excitement of the tough and anisotropic behaviour of polymer based composites [10, 11].

1.3. Blends and nanocomposites

SCORIM technique allows injecting different types of polymers and their blends. Unfortunately the immiscibility dominates in most polymer blends, including the incompatible nature of polypropylene, PP, with polycarbonate, PC, and usually requires compatibilization. In among of many methods of compatibilization, for instance, the reactive compounding, the mechano/chemical blending, the addition of a small quantity of co/solvent third component - miscible with both phases - is well explored options. This third component, like maleic anhydride-grafted polypropylene (MAP), can be use to improve adhesion between the phases [12, 13, 14]. Another recently suggested possibility for improved adhesion is the reinforcement with nanosized materials, like nanolayered silicates (e.g., montmorillonite). These nanofillers are incorporated into the matrix or in the composite to improve or modify optical, mechanical or physical properties. Nanocomposites of montmorillonite-polymer can be obtained by direct polymer melt intercalation or exfoliation. During this process polymer chains diffuse into the space between the clay galleries, and fully separated the clay nanolayers, respectively. Normally the apparent crystallinity increases with filler content and becomes asymptotic for more than 2-5% of the filler concentration [15].

In this study shear controlled orientation of injection moulding has been used to improve the mechanical properties of PP/PC composites and PP based nanocomposites.

2. Materials and methods

2.1. Materials

The basic polymeric materials used in this work were:

- (1) Polypropylene homopolymer (PP) type Moplen HP 501M from Basell with a density of 0.9 g/cm^3 ,
- (2) Polycarbonate (PC) type Lexan123R from GE Plastics with a density of 1.2 g/cm^3 ,
- (3) Maleic anhydride grafted polypropylene (MAP), Licomont AR 504 from Clariant, (MA content of 3.5 wt %) with a density of 0.91 g/cm^3 ,
- (4) Organo-modified nanoclay – layered silicates based on montmorillonite (nanoclay) type Nanofil 5 from Süd-Chemie with a density of 1.8 g/cm^3 .

Six different material compositions were studied:

- (a) neat PP
- (b) PP/MAP (97/3 wt%)
- (c) PP/NClay (97/3 wt%)
- (d) PP/PC (70/30 wt%)
- (e) PP/PC/MAP (67/30/3 wt%)
- (f) PP/PC/Nclay (67/30/3 wt%)

The percentage of nano-clay has been chosen according to supplier recommendations and to previous experimental work. Polymer ratio of 70/30 has been chosen in order to have a PP matrix (major phase) and based on literature results [16].

2.2. Specimens preparation

Before mixing, the PC was dried at 120°C during 4 hours (as recommended by the material supplier) in a dehumidifier (dew point of -40°C). PP as the matrix was mixed with the dispersive PC material in the fixed ratio of 70/30 wt%. The same blend has been also enriched by MAP and nanoclay in the ratio of 3 wt% of matrix. Mixing of the blends has been done in a rotational drum at the rotor speed of 60 rpm and at room temperature. The mixed blends were direct injection moulded in order to obtain $13 \times 8 \times 130 \text{ mm}$ rectangular specimens for flexural (ISO 178) and fracture (ASTM E399) tests. Neat PP has been prepared in the same way by CIM for comparison purposes.

2.3. Moulding programme

All compositions were injection moulded into rectangular bar specimens by using Ferromatik Milacron injection-moulding machine type K-85. Different settings of selected extreme operative variables were considered (Table 1).

Table 1.
Processing conditions used to obtain the bar specimens

Run	Stroke time (s)	Stroke number	Temp. profile ($^\circ\text{C}$) (from nozzle to hopper)
Min	1	3	240/230/220/210/200/40
Max	3	12	280/270/260/250/240/40

The temperature profile (T_p) was used in the processing set-up of the CIM technique. Two other parameters, namely the stroke time (St) and the stroke number (Sn), were also varied in the range of 1 to 3 s and 3 to 12 strokes, respectively. For all specimens injection pressure has been of 150 bar and kept constant, as well other parameters - holding pressure (50 bar), mold temperature (30°C), cooling time (30 s), injection velocity (15 mm/s).

2.4. Morphology characterization

The microstructures of the mouldings were observed by two experimental characterization techniques:

- a) thin microtomed slices of cross sections by polarized light microscope (PLM),
- b) fracture surfaces by scanning electron microscope (SEM).

PLM – Polarized Light Microscopy

For investigation of the samples, thinly cut films of $15 \mu\text{m}$ of thickness have been prepared, from the specimens cross sections perpendicularly to the flow direction. These thin slices were observed by polarized light microscopy to evaluate micro structural differences and the dispersion of the disperse phase.

These analyses have been performed on an Olympus light microscope type BH2 additionally equipped by the Olympus digital camera DP11. High resolution of the photos was required for efficient recognition and counting the layers. Interactive image analyser computer software Quantimed 500C has been used for counting the thickness of layers.

SEM – Scanning Electron Microscopy

Scanning micrographs of the fracture surfaces of the specimens could bring better look on the differences between the core, shear zone and outer skin energy absorption, by evaluation of the level of the roughness or smoothness of the surface. All fractographic investigations have been executed on SEM Leica Cambridge type S 360 at voltage of 15 kV. Specimens were previously coated by a thin layer of gold.

2.5. Mechanical characterization

The flexural tests were performed in an Instron universal mechanical testing machine type 4505 at the crosshead velocity of 10 mm/min in conformity of ASTM E399 at temperature of 23°C and relative air humidity of 50%. Notch with depth of 6.35mm was machined in a Ceast cutting notch machine type 6816 with the blade 6530 with a blade radius of 0.47 mm. The notches were then sharpened deeply by a razor blade. At least five specimens have been analysed for each test.

3. Results and discussion

3.1. Morphology development

Fig. 4 is representative of the cross sections of the mouldings as observed by PLM and SEM, showing the skin/core structure for conventionally injected specimens and the typical layered structure of melt manipulation technique.

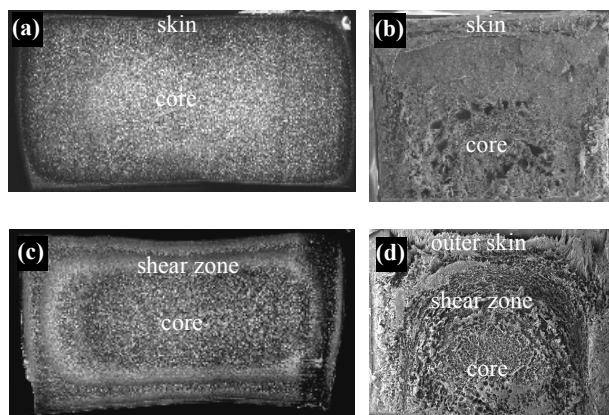


Fig. 4. Cross section of the PP/PC specimen by PLM and SEM; (a, b) conventional technique, (c, d) SCORIM technique

Main difference between techniques can be observed from the photographic matching. As shown, the SCORIM samples feature a thick shear zone, which contains many oriented layers. Polarized light enables to investigate the shape, number and thickness of the layers.

3.2. PP Nanocomposites

In Fig. 5 are presented the microstructures of the neat PP, PP/MAP and PP/NClay nanocomposites. The effect of the processing parameters is clearly seen, a multilayered structure been observed for the high settings. Addition of nanofillers (MAP and NClay) diversified the morphology, especially developing the shear zone as shown in Fig. 5. d) and f).

Comparison of differences between the thicknesses of the layers also has been done. Example of the counting is presented on magnified image (Fig. 6), where the layers are identified. Fig 7 compares the number and thickness of each layer for all the specimens.

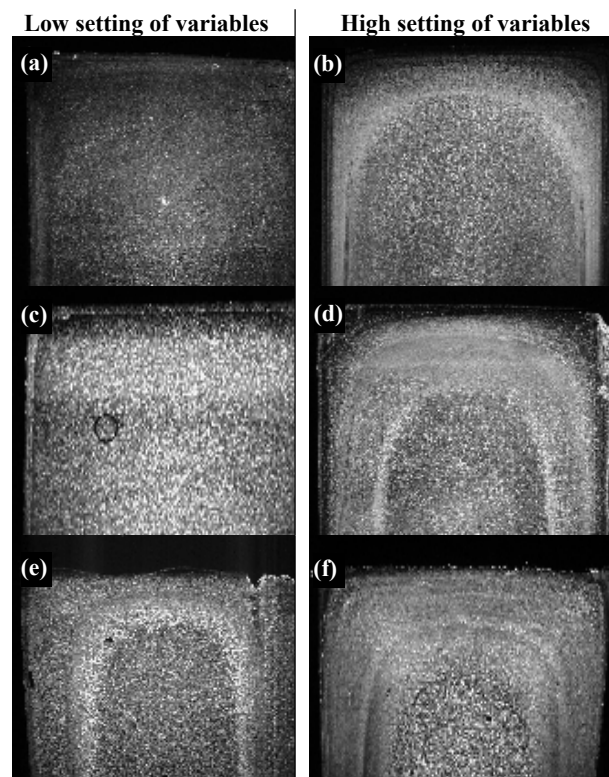


Fig. 5. PLM photos of different PP composites under extremes conditions: (a) PP at 1st run, (b) PP at 8th run, (c) PP/MAP at 1st run, (d) PP/MAP at 8th run, (e) PP/Nanoclay at 1st run, (f) PP/Nanoclay at 8th run

At higher setting of processing conditions, well forming of the layers has been observed. Under the same run different composites had diversify capability of forming the layers. The manipulation of the processing parameters changes the lamination

of the layers, depending upon the type of reinforced polymer. High setting variables contain much more layers than low settings. Best example is the case of PP/NClay, where the number of layers is 8 in the high setting run that is 4 times more than for the opposed processing settings. The skin thickness for the same nanocomposite is more than 2.5 times thicker for the lowest settings.

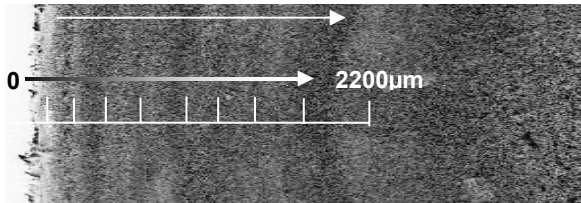


Fig. 6. PP/Nanoclay for 8th run – thickness of layers at higher magnification (the same as Fig. 5 f)

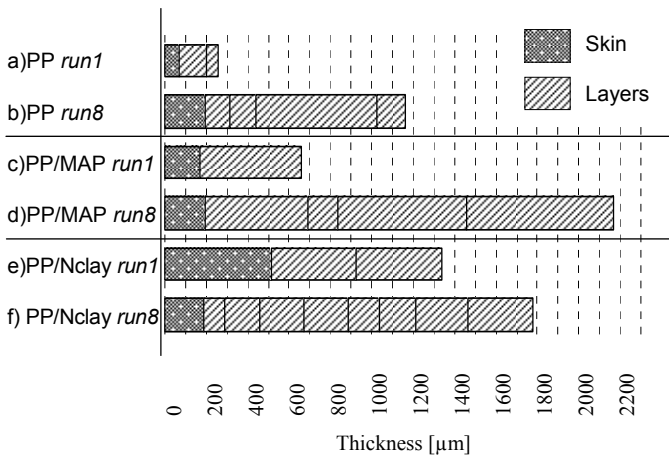


Fig. 7. Thickness of layers for all molded specimens (numbering according to the photographs of Fig. 5)

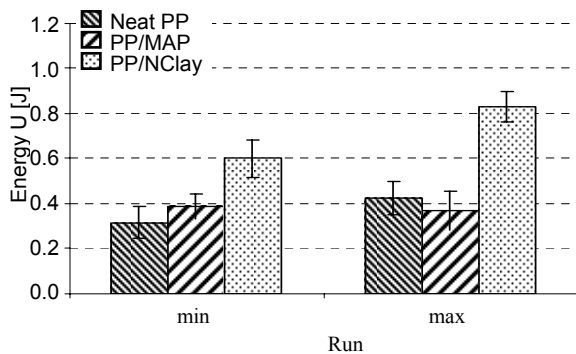


Fig. 8. Fracture energy of PP composites for min-max processing set-up

3.3. Fracture behaviour

Fracture energy of PP systems was essentially higher for high processing level, as shown in Fig. 8, except for the case of PP/MAP that is insensitive to processing. PP/NClay gives the highest results, especially for maximum run. Adding the compatibilizer has a slight influence on the energy absorption capabilities.

The fracture surfaces for both PP and PP/MAP were smooth (Fig. 9 a-d). PP reinforced by nanoparticles show different behaviour at low processing conditions setting (run 1) and its fracture surface is rough (Fig. 9 e), showing the highest fracture energy. The fracture surface of Run 8 of this nanocomposite presents a lower roughness but spread over all the specimen cross section (Fig. 9 f). The increase on the fracture toughness is related to a higher sustained stress level than to a higher ductility.

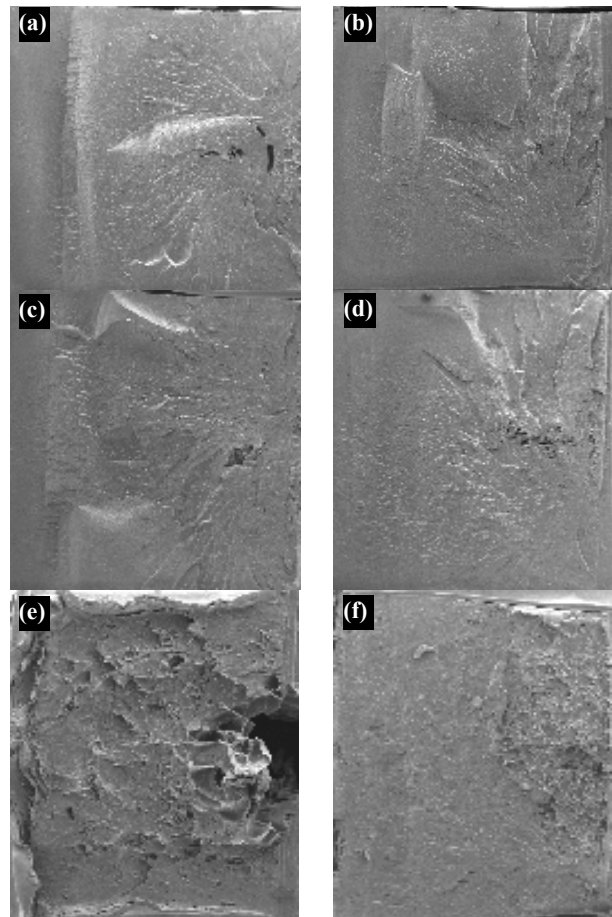


Fig. 9. SEM micrographs of different PP nanocomposites under extreme moulding conditions: (a) neat PP at 1st run, (b) neat PP at 8th run, (c) PP/MAP at 1st run, (d) PP/MAP at 8th run, (e) PP/NClay at 1st run, (f) PP/NClay at 8th run

Composites of PP/PC and its reinforced types feature more diversified morphology as shown in Fig. 10. Mostly for high setting of the processing variables of PP/PC composites, the

structure is more distinctly formed than for the opposed adjusted variables. The oriented shear zone clearly is recognized on the SEM micrographs. Focusing attention on high-settings injected samples of PP/PC, it can be observed multiple layers surrounding the core (Fig. 10 b). This microstructure is originated from the number of strokes and their long hold mean time. Approximate similarities occur in the PP/PC/MAP, where the core is almost perfectly separated from the shear zone, and the PP/PC/NClay, where nanoparticles strong facilitate the forming of the visible layers (Fig. 10 d, f).

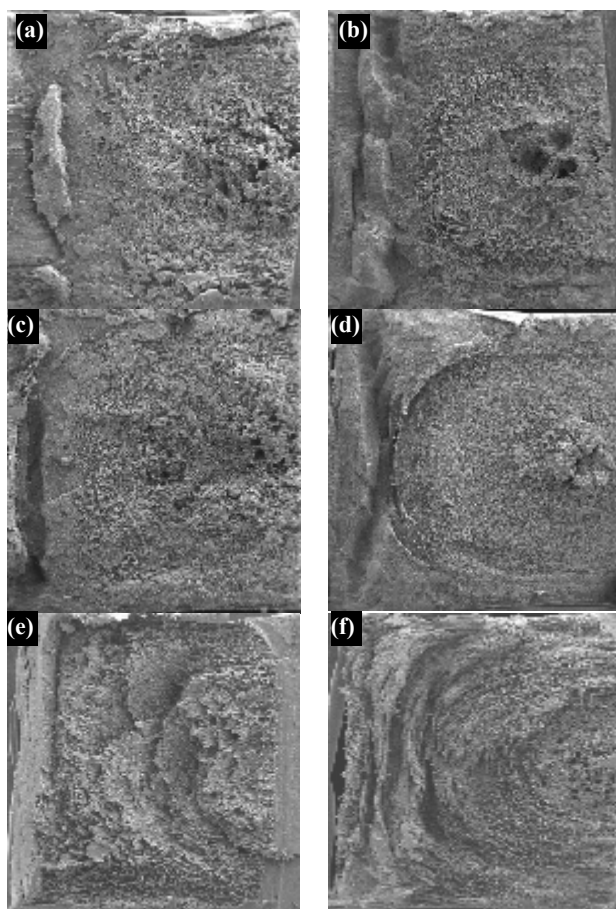


Fig. 10. SEM micrographs of different PP/PC composites under extremes conditions: (a) PP/PC at 1st run, (b) PP/PC at 8th run, (c) PP/PC/MAP at 1st run, (d) PP/PC/MAP at 8th run, (e) PP/PC/NClay at 1st run, (f) PP/PC/NClay at 8th run.

Fig. 11 shows the energy results for the PP/PC composites. There is a significant increment on the fracture energy for pure PP/PC composite over neat PP, in spite of PP/PC blend being immiscible. Miscibility has meaningfully influence on the composite strength. If the bonding between the two phases is weak the strength is less. This however seems to be beneficial for toughness. In fact the comparison between both fracture surfaces (Fig. 9 and 10) reveals that PP yields more locally when blended with PC consuming more energy. The addition of 3% of compatibilizer did not improve the mechanical behaviour at low

processing settings. For high processing settings, there is a decrement on the fracture energy. The fracture surfaces are visibly different, evidencing different mechanism of energy dissipation during fracture. Shifting to last composition, PP/PC/NClay, it is visible that similar tendency is maintained. Fracture energy is significantly lesser for PP/PC/Clay than for PP/NClay. The addition of the nanoclay to PP seems to affect its ductility (see fracture surfaces on Fig. 9 e) and f) dissipating high energy levels during fracture. In the case of the nanofilled blend, a more brittle failure is obtained.

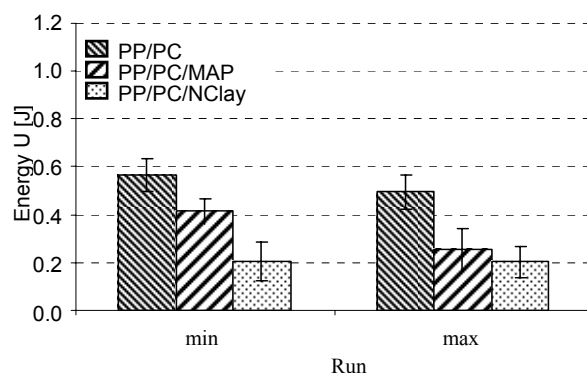


Fig. 11. Fracture energy of PP/PC composites for min-max setting of processing conditions.

Immiscibility and the higher viscosity of the PP/PC blend didn't allow a good dispersion of the nanoclay, even at higher processing setting. The fracture surfaces of the PP/PC/NClay blends reflect well the different microstructures of the developed layers (compare to the microstructures of Fig 5 e) and f). The nanoclays seems to be distributed differently in this layers. Further work on this area is necessary for better understanding the development of morphology. This is in progress.

4. Conclusions

1. The hydraulic pistons movement during SCORIM cycle influenced on multilayer structure. For PP specimens, the shear zone of high-setting adjustment was nearly 4 times more developed than in the low-setting of processing variables. Addition of nanoparticles to PP did not change extremely the dimensions of this zone, but increased the number of layers.
2. Nanoparticles induce forming a multilayer structure, especially at higher melt temperature.
3. The energy absorbed by specimen of PP/NClay was 3-fold higher than in the neat PP and PP/MAP.
4. Melt temperature, stroke time and number are determinant of the fracture energy of the neat PP. Higher setting of these processing variables gives enhanced fracture energy (25% higher).
5. Immiscible polymer blends PP/PC processed by melt manipulation techniques show improved fracture toughness compared to neat PP.

6. Addition of MAP to PP/PC did not affect the fracture energy for low setting of the processing variables, but significantly decreased it for high adjustments.
7. Addition of nanoclay to PP/PC is detrimental for the fracture energy of the mouldings.

Acknowledgements

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