

Self reinforced polymer-polymer composites

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Materials

ABSTRACT

Purpose: Purpose of this paper is the applying of new technology in injection moulding technique and investigation of reinforcement of PC as dispersed phase inside PP matrix (Table 1). Second aim of work is enrichment of those composites by nanoclay and analyzing mechanical behaviour of nanocomposites.

Design/methodology/approach: According to design of experiments (DOE) specimens were injection moulded in the shape of rectangular bars. Additionally advanced technology of melt manipulation inside mold cavity after injection was used. To achieve this purpose Ferromatik Milacron injection moulding machine, equipped with externally controlled mold was used.

Findings: Addition of nanoclay clearly presents highly reinforced system, especially for neat matrix. Evenly dispersed PC particles within PP majority show reinforcement as well. Inducement of shear rate in injection moulding radically improved absorption of energy in nanocomposite.

Research limitations/implications: Different variation of material composition, such combination with other polymers and use of different reinforcements (flexible or either rigid) is required to be checked in the further work.

Practical implications: Reinforcement obtained thanks to dispersed phase and nanofillers creates composites with improved mechanical properties.

Originality/value: Morphology development reflects on mechanical behaviour. Its manipulation may affect and improve mechanical properties. Use of advanced technologies opens wide range of possibilities in processing of polymer based systems. At present there is limited number of research of processing-structure-properties relationships of polymer-polymer composites and nanocomposites.

Keywords: Polymer-polymer composites; Injection moulding; Microstructure; Fracture properties

1. Introduction

Structure imposed due to thermal and mechanical injection moulding processing influence mechanical behaviour of obtained material or composite [1, 2, 3]. Manipulation of applied shear may bring efficient results in mechanical improvement and structure development [4, 5, 6]. Simultaneous combination of material's composition can affect deformation capabilities of the material. Advanced injection

moulding techniques manipulate solidifying polymer inside mold cavity [7, 8, 9]. It creates highly oriented multilayered structures with, repeatedly, enhanced mechanical properties [10, 11]. In a recent route many reinforcements have been used in polymer systems like fiberglass, micro-, nanoparticles (e.g. MMT – Table 1) to advance their properties [2, 12, 13]. Polymer nanocomposites are a worldwide research area in the last decades, namely those based on layered silicates. The amount of nanoparticles in a polymer nanocomposite can vary at different ratios. Generally, for the sake of high cost of

Table 1.
Abbreviations

Material		Processing	Analyzing		
Montmorillonite	MMT	Conventional Injection Moulding	CIM	Light Polarized Microscopy	PLM
Polypropylene	PP	Non-conventional IM	N-CIM	Scanning Electron Microscopy	SEM
Polycarbonate	PC	Shear Controlled Orientation in IM	SCORIM	Notch depth	A
		Melt temperature	T _m	Specimen width	W
		Stroke time	ST	Specimen thickness	B
		Stroke number	SN	Fracture toughness	J ₀

nanofillers, filling is employed up to 5% of nanoclay [14]. Polymer-nanoclay interaction can increase stiffness and fatigue of materials. However, ratios of nanoparticles up to 10% has been reported [15], nevertheless their incorporation can be reduced to few percent due to their large contact surface area [16]. It can be bravely notified, that polymer-polymer reinforced nanocomposites processed by different techniques are attractive direction to obtain high mechanical performance polymeric materials.

2. Materials and processing

2.1. Materials

PP has been used as major phase (matrix) and PC as the dispersed phase in the minority. They were mixed at the ratio 70/30 wt% of PP/PC. Nanoparticles were blended in the ratio 67/30/3 wt% (PP/PC/MMT). Materials were blended in a rotation barrel at the constant speed of 60 rpm. All materials are specified in the Table 2 below.

2.2. Processing

Experiment bases on two types of injection moulding techniques: a) conventional injection moulding (in the aim of comparison results with another technique), b) melt manipulation injection moulding technique, SCORIM. A Ferromatik Milacron type K-85 injection moulding machine was used, equipped with a special mounted SCORIM mold with manifold and hydraulic system. All specimens were injection moulded (under stabilized injection parameters) into rectangular bars with dimensions of 130x13x8 mm, laterally gated at two extremities.

The molding programme was defined according to a design of experiments (DOE) approach. Based on the 3-factorial, 2-level array, experiments followed the 8-run table (Table 3), which contains 2 extreme values for each changeable processing parameter. It has been done to include terminal mechanical behaviours of composites.

Three changeable processing parameters were considered in the molding programme: the melt temperature mutual for both injection molding techniques, stroke time and number in the case of SCORIM. Injection pressure, exerted by screw into the cavity, as well as other parameters, was kept constant (Table 4).

Table 2.
Materials' specifications

Materials	Grade/Supplier	Characteristics
Polypropylene	Moplen HP 501M, Basell	density: 0.9 g/cm ³ , melt temp: 200°C
Polycarbonate	Lexan 123R, GE	density: 1.2 g/cm ³ , melt temp: 240°C
Montmorillonite	Nanofil 5, Süd-Chemie	density: 1.8 g/cm ³ , melt temp: >390°C

Table 3.
Variable injection processing set-up for N-CIM

Processing parameter	RUN			
	<i>Low ST-SN setting</i>			
	1	2	3	4
ST	1	1	1	1
SN	3	3	12	12
T _m	240	280	280	240
	<i>High ST-SN setting</i>			
	5	6	7	8
ST	3	3	3	3
SN	3	3	12	12
T _m	280	240	240	280

Table 4.
Constant injection processing set-up

Cooling time	30 s
Mold temperature	30 °C
Holding pressure	50 bar
Injection pressure	150 bar
Injection velocity	10 mm/s

2.3. Mechanical characterisation

Specimens (at least five per test) were tested by 3-point bending test with crosshead speed 10 mm/min (according to the ASTM E399 standard) at room temperature (23 °C) and constant humidity (50%) on universal testing machine Instron type 4505. Fractured specimens were previously notched in a Ceast notch cutter type 6816 with a notch depth of a = 6.35 mm and then sharpened with razor blade. Polymer-polymer composites and nanocomposites were mechanically tested in the aim of observations the influence of processing conditions over fracture behaviour.

The fracture toughness was calculated by a J-integral value, J₀, directly derived from the integration of the load-displacement diagram via the total energy, U:

$$J_0 = \frac{\eta_e U}{B(W-a)} \quad (1)$$

where, η_e is a geometric factor ($\eta_e=2.03$ for a single edge notched beam, SENB, for $a/W=0.5$), B and W are the specimen thickness and width, respectively and a is the notch depth.

3. Results

Figure 1 presents distribution of PC particles inside PP matrix. Specimens were etched by cyclohexanone for 24 hours to solve PC particles (visible caving) and treated by computer aided image analysis (Fig 1.). Analysis confirmed presence of 26% hollow area confirming well distribution of dispersed phase.

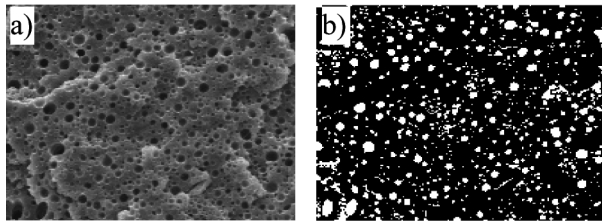


Fig. 1. a) SEM micrograph of PP/PC composite etched in cyclohexanone, b) image analysis of caving area

Figure 2 below presents the variations of the fracture toughness of the polymer systems processed by CIM.

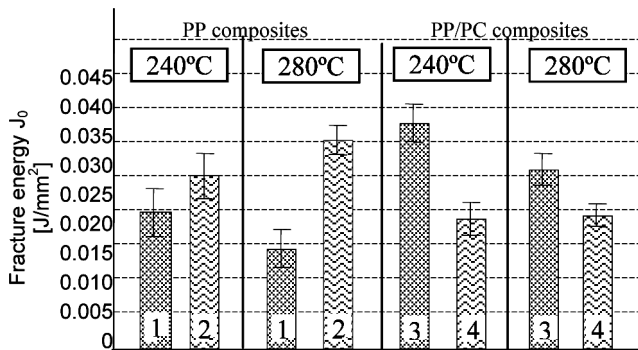


Fig. 2. Fracture toughness of the materials systems processed by CIM, where 1 - PP, 2 - PP/MMT, 3 - PP/PC, 4 - PP/PC/MMT

The addition of the nanoclay to the pure PP improved the fracture toughness, mainly for the $T_m = 280^\circ\text{C}$. Moulding 1 at low temperature presents higher J_0 value than this one injected at higher temp. This can happen due to low degree of crystallinity (low melt temperature), evidencing therefore superior fracture toughness. Further WAXS analysis may confirm it. For the PP nanocomposites, the increment on the melt temperature leads to an increase on J_0 values. High melt temperatures should assure better exfoliation and in effect promotes less nanoclay agglomeration.

The pure PP/PC blend shows high fracture behavior at both melt temperatures (a maximum value of 0.032 J/mm^2). However, the addition of MMT to this polymer-polymer composite greatly reduces the fracture toughness. Nanoclusters spread together with PC particles could affect stress concentration and weaken composition.

Fig. 3 shows the variations of the fracture toughness of pure PP and PP/PC blend with the processing conditions for N-CIM. Results presented on graph are divided in two sections accordingly to low and high T_m . The x-axis illustrates the respective of the number and time of piston movements (strokes). The melt manipulation during solidification alters significantly the fracture toughness of the mouldings.

Variation of J_0 in N-CIM is 109.1% for pure PP and 97.4% for PP/PC blends. For pure PP, the mouldings obtained with low T_m

shows higher J_0 values. The increment on ST and SN increases the fracture toughness of the mouldings, especially for low T_m . The maximum fracture energy originates from 7th run (low T_m , high ST and high SN; Table 3) resulting J_0 value of 0.022 J/mm^2 .

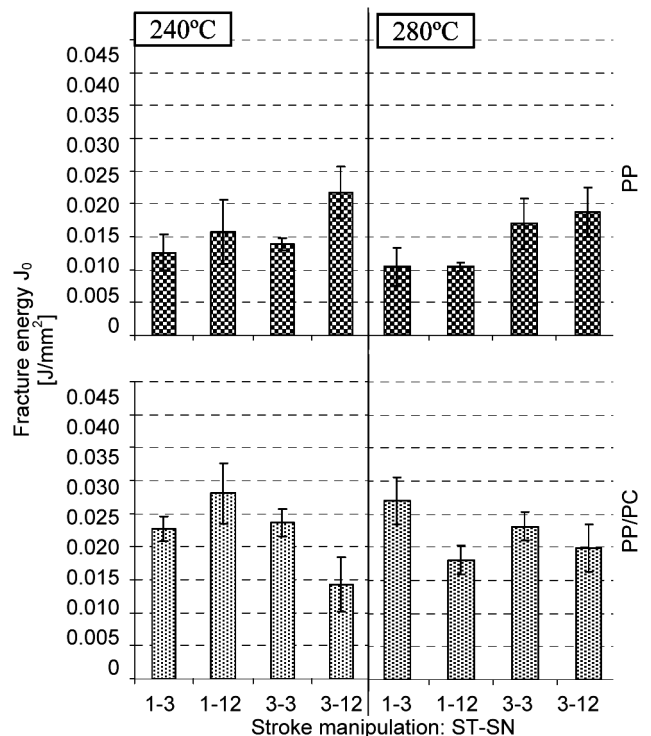


Fig. 3. Fracture energy of composites for low and high temperature settings of N-CIM

PP/PC blend presents higher values of J_0 for all conditions compared with the neat PP (except for run 7th, where the pure PP shows the maximum J_0). This is more evident for the specimens molded with low ST. The maximum difference comes from the 2nd run with an improvement of 159.3% compared with the pure PP. The maximum J_0 for the PP/PC blend is from the 4th run ($T_m = 240^\circ\text{C}$, ST = 1, SN = 12) with 0.028 J/mm^2 (27% higher than the maximum J_0 of PP).

Fracture toughness results for the MMT added to composites and processed by N-CIM are presented below (Fig. 4). The change of the processing conditions in N-CIM induces variations on J_0 values of 83% and 241.5% for PP and PP/PC blend. This latter result arises from the significant lower values of J_0 evidenced by the PP/PC/MMT blends. The addition of 3 wt% of MMT increases noticeably the fracture toughness of the neat PP (240% for 2nd and 6th run). The maximum J_0 is obtained for combination of low T_m /high ST/low SN. On the contrary to CIM mouldings, N-CIM's fracture toughness improved for low T_m (and high shearing time), where a high level of orientation should be induced due to the low melt temperature.

For the PP/PC nanocomposite the fracture response is much lower, this material composition showing the lowest J_0 values. The maximum J_0 is of 0.020 J/mm^2 , which is similar to the same blend processed by CIM ($J_0 = 0.019 \text{ J/mm}^2$). Processing this blend by N-CIM is detrimental for the fracture toughness of the material (even worse than PP/PC/MAP).

Table 5.

Maximum J_0 values, for all PP based material systems

Material composition	N-CIM		CIM		Variations induced by:		
	T_m /ST/SN	J_0	T_m	J_0	processing	composition* in N-CIM	composition* in CIM
	[°C/s/]	[J/mm ²]		[J/mm ²]	[%]	[%]	[%]
PP	240°C/3/12	0.022	240°C	0.020	10.0	0.0	0.0
PP/MMT	240°C/3/3	0.048	240°C	0.030	60.0	118.2	50
PP/PC	240°C/1/12	0.028	240°C	0.032	-12.5	27.3	60
PP/PC/MMT	280°C/1/3	0.020	240°C/280°C	0.019	5.3	-9.1	-5.0

* with respect to pure PP

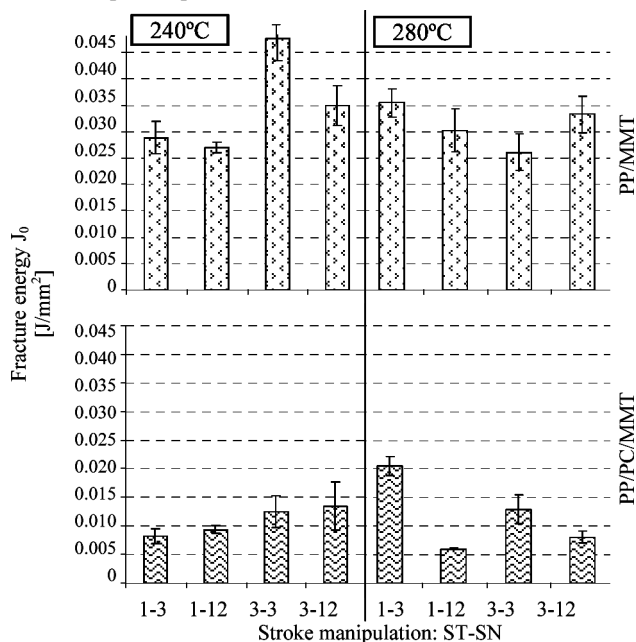


Fig. 4. Fracture energy of composites for low and high temperature settings of N-CIM

4. Conclusions

1. Addition of nanoclay clearly presents highly reinforced system, increasing fracture toughness, especially for neat matrix. Maximum J_0 values for PP belong to the 6th run in the low temperature range.
2. Higher improvement on J_0 comes from PP/MMT processed by N-CIM (Table 5).
3. CIM technique brings higher energy absorption for PP/PC.
4. Specified processing conditions induce a thicker multilayered highly oriented skin zone. This investigation requires further work.

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