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Toughness distribution in complex PP/nanoclay injected mouldings

Valeria Pettarin [a,*], Florencia Brun [a], Julio C. Viana [b], Antonio S. Pouzada [b], Patricia M. Frontini [a]

[a] *INTEMA Institute of Materials Science and Technology, University of Mar del Plata, A. Juan B. Justo 4302, B7608FDQ Mar del Plata, Argentina*
[b] *IPC/Institute for Polymers and Composites, University of Minho, Guimaraes Codex PT4800-058, Portugal*

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ABSTRACT

The fracture performance of PP–nanoclay box-like injection mouldings obtained in double gated mould and by direct compounding of PP and a PP-based masterbatch was studied. Samples were observed by polarised light microscopy and characterised by DSC. Other samples were fractured using mode I double edge-notched tensile specimens. Their typically brittle fracture did not show neat in-plane crack propagation. The initial crack was branched and deviated out of the plane normal to the applied stress, and the fracture no longer followed the simple mode I. There is a tendency towards increasing the ductility and the deformation at break with the increase in nanoclay content. The fracture initiation does not depend on the nanoclay content or on the test piece location; nanoclay reinforcement increases the energy propagation release rate, G_{cp}, away from the weld line. The results allow the proposal of a model for the micromechanisms acting in samples which in-turn depends on nanoparticle orientation.

1. Introduction

Propylene homo and copolymers (PP) are common materials for industrial automotive applications due to their many advantageous properties that include broad portfolio, low density, environmental stress-cracking resistance, unique ability to form integral hinges, price and ability to be readily recycled. Nonetheless, the application of pure PP in automotive is somewhat limited by its poor mechanical properties (such as tensile strength and impact resistance), scratch resistance or pre-treatment often required for painting [1].

In the last decade nanocomposites based on thermoplastics modified with nanoclays emerged as a topic of industrial and academic interest [2–4]. These nanocomposites have been reported to exhibit visible improvements when compared with the corresponding raw materials and micro- and macro-composites [5]. However it is been claimed that only well-dispersed and well-exfoliated nanoparticles can lead to the expected improvement of properties [6]. Raw material producers, converters and end-users have tackled both compounding and processing issues, usually resorting to the surface modification of nanofillers with organic surfactants and adaptation of compounding conditions to get rid of most of compounding issues. The development of masterbatches has reduced the health and safety hazards. The final injection or extrusion moulded parts may be easily obtained by mixing/diluting the masterbatch with the appropriate polymer matrix. The nanoparticle dispersion (and exfoliation where applicable) is usually assumed to be achieved during the masterbatch compounding.

Most PP-composites are processed by an injection moulding process. The injection moulding process involves the injection of a polymer melt flow into a mould impression where the melt cools and solidifies to form a plastics product. It is a three-phase process comprising filling, packing, and cooling. The occurrence of weldlines is a major design concern as weldlines could lead to a considerable reduction in mechanical properties; in consequence designers often need to incorporate liberal safety factors in design analysis to compensate for this weakness. Weldlines are often observed in injection moulded components due to multigate moulding, existence of pins, inserts, variable wall thickness and jetting and are classified as either being cold or hot. The cold weldlines are formed when two melt fronts meet head on and this type of weld provides the worst-case scenario as far as mechanical properties are concerned. While weld lines can be deleterious in homopolymer mouldings, the problem can be amplified in two-phase systems, such as reinforced thermoplastics [7]. For example, whilst the addition of spherical shaped fillers (e.g. glass spheres) has shown to have little effect upon tensile strength of injection moulded thermoplastics with weldlines, the addition of large aspect ratio fillers (e.g. short fibres) led to a considerable reduction in weldline strength due to the alignment of the fibres parallel to the weldline.

The understanding of the fracture, microdeformation and mechanics of nanocomposites is rather vague. Although claims are made that the mechanical properties of nanocomposites should be excellent, in practice the mechanical properties are often disappointing [8–12]. Cotterell and co-workers suggested that the orientation of the clay particles during injection moulding is

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* Corresponding author. Tel.: +54 223 481 6600x183; fax: +54 223 481 0046.
E-mail addresses: pettarin@fi.mdp.edu.ar (V. Pettarin), jcv@dep.uminho.pt (J.C. Viana), asp@dep.uminho.pt (A.S. Pouzada), pmfronti@fi.mdp.edu.ar (P.M. Frontini).

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in part responsible for the embrittlement of semicrystalline polymers by nanoclay particles [13]. Much work has been done characterising injection moulded thermoplastic nanocomposite specimens [10,14–22]. However, as far as the authors know, there is no study of mechanical properties on actual PP–nanoclay mouldings, in which a complex orientation field and weld lines occur, and consequently it might be a distribution of properties.

In the case of the common mechanical properties such as the Young's modulus or the yield strength the testing techniques are simple and require little thought or interpretation. On the other hand, toughness is a more difficult property to characterise. In the past, the Izod or Charpy impact energies have been used to characterise toughness. In industry these types of tests continue to be used as an economical quality control method to assess the notch sensitivity and impact toughness of polymers. It has long been recognised that the impact energy is a complex strain rate function of the plastic and fracture work, the plastic work being generally dominating. The Izod and Charpy tests have lost favour in engineering design because they cannot be used directly in the calculations. In their desire to characterise toughness of ductile polymer nanocomposites more exactly, many researchers have turned to fracture mechanics (e.g. [13,23,24]).

Through this work it was studied the fracture performance of PP–nanoclay composite injection moulded parts obtained by direct compounding of a commercial PP and a PP based masterbatch (MB). A double gated mould was used, in which a weld line is formed by melt fronts meeting at different angles, and a distribution of molecules and particles orientation is generated from the injection points. The influence of singularities induced by flow pattern such as weld lines and injection points, as well as MB content on the arrangement of mechanical performance in the moulding were explored.

2. Experimental

2.1. Materials and processing

The study was conducted on propylene homopolymer, F-045 D2 (from Sunoco Chemicals) with MFI of 4.9 g/600 s at 230 °C, and a commercial MB of PP with 50% of organoclay, Nanomax-PP P-802 (from Nanomax Polyolefin Masterbatch Products).

The nanocomposites were obtained by direct injection of mixtures of PP and MB. Various amounts of nanoclay incorporation were used by mixing 2%, 6% and 10% of MB with PP, these mixtures being referred to hereon as PP-1, PP-3 and PP-5. Rectangular boxes of 1.4 mm thickness (Fig. 1) were injection moulded in a double-gated hot runner injection mould using a Klöckner Ferromatic FM20 injection machine with 200 kN clamping force. The processing setup is listed in Table 1.

2.2. Characterisation

2.2.1. Morphology

The global crystallinity of the material in the mouldings, that influences the mechanical properties, was determined after differential scanning calorimetry (DSC) tests on specimens that involve the whole skin–core structure. Tests were performed in a Perkin Elmer Pyris 1 device using 10 mg nominal sample weight, at a scanning rate of 10 °C/min from 50 °C to 200 °C under nitrogen atmosphere. The crystallinity was calculated as:

$$x_c = \frac{\Delta H}{(1-\phi)\Delta H^0} \qquad (1)$$

where ΔH is the apparent enthalpy of fusion of the composite, ΔH^0 is the heat of fusion of 100% crystalline PP which is of 207.1 kJ/kg [25], and ϕ is the weight fraction of MB in the composites.15 μm-thick specimens were microtomed with a Leitz 1401 microtome and observed with an Olympus BH2 microscope using polarised light.

XRD analysis was performed on samples from the skin layer using a Phillips X'PERT MPD diffractometer (Cu Kα radiation λ = 1.5418 Å, generator voltage = 40 kV, current = 40 mA). Measurements were recorded every 0.02θ for 1 s each varying 2θ from 5° to 40°.

Scanning electron microscopy (SEM) was applied to observe cryofractured injection moulded specimens using JEOL JSM-6460 LV equipment

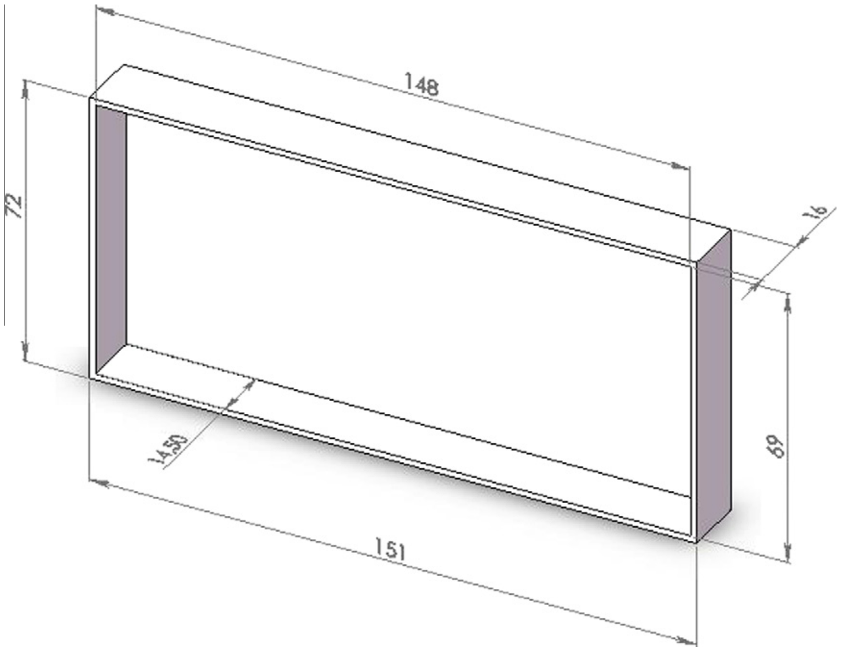

Fig. 1. Scheme of mouldings with their dimensions.