IMPACT BEHAVIOR OF INJECTED PP/NANOCLAY PARTS

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This work attempts to contribute to bridge the gap between scientific challenges and industrial stakes regarding PP/nanoclay composites. Pieces of nanocomposites were obtained by direct injection of commercial PP mixed with a commercial MB of PP with 50% of organoclay, with a double-gated hot runner mould, which produced mouldings with a weld line. The moulding microstructure was assessed by POM and XRD, while the distribution and exfoliation grade of clay was evaluated by TEM and XRD. The typical skin-core structure was found, with a skin thickness wider in bulk than in weld line zones. Regarding clay platelets mostly intercalated structures were seen. The impact properties at room temperature were assessed by means of tensile and biaxial tests. Properties were monitored at different sites of the mouldings. At the weld line zone less energy was consumed under tensile conditions and exhibited higher apparent impact toughness under biaxial conditions than the bulk zone. Visual inspection of biaxially impacted samples showed that the orientation of polymer molecules and clay platelets induced by melt flow prevailed, and the weld line was not the determinant of the toughness of the mouldings. An optimum in impact performance was found for moulding with 3% of clay, since at larger clay contents platelets agglomerated and acted as stress raisers.

Introduction

Polypropylene (PP) belongs to the group of thermoplastics produced in large quantities. Great efforts are undertaken to transform PP into a thermoplastic suitable for engineering use. Research work has therefore been focused on upgrading the mechanical performance of PP by toughening (to overcome the moderate cold and impact resistance) by filling and reinforcing (to increase stiffness, strength and temperature resistance and to decrease shrinkage) or both (Karger-Kocsis, 1993).

Polymeric nanocomposites have emerged as new materials showing potential for industrial application and quite exceptional properties at low filler contents (Ray and Okamoto, 2003; Alexandre and Dubois, 2000). The interest in polymer/layered silicate nanocomposites is still large and intensive research is going on in many research groups in this field in spite of the fact that a real breakthrough has not been achieved yet.

An important commodity polymer such as PP, when filled with a low incorporation level of nanoclay (typically less than 5%), can be used in applications with requirements typical of engineering plastics with additional advantages. However, only well-dispersed and well-exfoliated nanoparticles can lead to the expected improvement of properties (Zhang et al, 2004; Ding et al, 2005; Chen et al, 2000). Raw material producers, converters and end-users have therefore to tackle both compounding and processing issues. Surface modification of nanofillers with organic surfactant and adaptation of compounding conditions (high shear, high residence time, special screw profile design in case of melt compounding for example) may help to get rid of most of compounding issues. Research groups have made significant progress in that field. With the development of masterbatches (MB) the final injection – or extrusion – moulded part should be easily obtained by mixing/diluting the MB in the appropriate polymer matrix. The nanoparticle dispersion and exfoliation is usually assumed to be achieved during the MB compounding. Experience unfortunately often shows that the industrial reality is quite different (Krawczak, 2007).

Injection moulding is the most important process to manufacture plastic parts, since complex geometries become available in one automated production step. Nonetheless, the influence of processing parameters is critical in the performance of these products (*e.g.* Cunha and Pouzada, 1995). Moreover, if weldlines are likely to occur in injection moulded products, things become more complicated. Weld lines are an unavoidable reality in the injection moulding of complex parts. Multiple gating, splitting of the melt flow due to inserts in the cavity or through holes, as well as changes of thickness give rise to regions in the impression where the melt flow fronts recombine and weld. Weld lines are formed along with the mould filling process: particularly in the moulding of very complex components a multiplicity of weld lines is generated. In the region were weld lines occur the properties are different from the bulk (Ersoya and Nugay, 2004; Morelli et al, 2007). Whereas the complete elimination of weld lines is not always successful, their adverse effects on part appearance and mechanical performance can be minimized by changing mould design and process conditions (Wu and Liang, 2005).

Impact strength is often one of the fundamental material requirements used to measure the performance of plastics products. Falling-dart impact tests on disc or plate specimens are widely used by the plastics industry to characterize the “practical” resistance of rigid thermoplastics, because they are intended to reproduce the real behaviour of moulded parts under impact loading. They are product tests on representative components, rather than measurements of basic material properties. One additional advantage of the falling-dart impact test is that it provides a convenient method for studying changes induced by flow modification in part performance (Cunha et al, 1997; Bucknall, 2000).

This work attempts to contribute to bridge the gap between scientific challenges and industrial stakes regarding PP/nanoclay composites. Impact behaviour of PP/nanoclay injection moulded parts obtained by direct compounding of commercial PP and MB was studied. Influence of processing parameters and weld lines on in-plane and out-of-plane impact behaviour was explored.

Experimental

Materials

This study was carried out on a propylene homopolymer, F-045,D2 (from SUNOCO Chemicals) and a commercial MB of PP with 50% of organoclay, Nanomax-PP P-802 (from Nanomax Polyolefin Masterbatch Products).

Injection moulding

Nanocomposites were obtained by direct injection of mixtures of PP and MB. Different amounts of incorporation of nanoclays were used by diluting the MB in the PP matrix. 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 of 200 kN clamping force. The injection pressure was monitored during injection. The processing conditions are listed in Table 1.

The Taguchi method (Rosse, 1996) was applied to determine the effect of moulding parameters on the impact behaviour of pieces. Three moulding parameters were selected: masterbatch content (MBp), melt temperature (Tm), and injection speed (Qj). Because the influence of these factors may vary non-linearly, each factor was assigned with three levels. According to the levels of each parameter, an L9-orthogonal table was used to inject the pieces (Table 2). The nine conditions were repeated with pure PP mouldings for comparison. Additional pieces were injected according to experiment #2 with various MBp contents (2, 6, 10 and 14%).

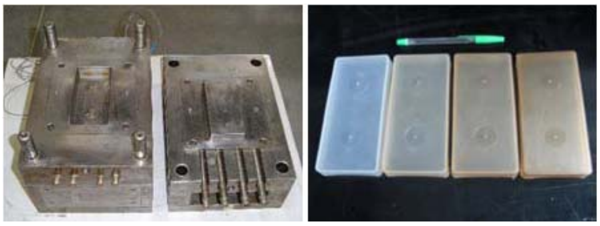

Figure 1 – Hot runner mould and PP/nanoclay mouldings.

Table 1 – Processing settings

Processing parameter	Value	
Barrel temperature	Zone 1	160ºC
	Zone 2	185ºC
	Zone 3	215ºC
	Zone 4	235ºC
Screw rotation velocity	250 rpm	
Injection pressure	5 MPa (50 bar)	
Injection time	1 s	
Packing pressure / time	3 MPa, 10 s	
Cooling time	15 s	

Table 2 – Design of experiment and factors and levels for the injection moulding experiments

Experiment #	MBp (%)	Tm (ºC)	Qj (mm/s)
1	6	205	100
2	6	220	350
3	6	235	400
4	10	220	400
5	10	235	100
6	10	205	350
7	14	235	350
8	14	205	400
9	14	220	100

Microstructure

Polarized light microscopy was used to observe the morphology of mouldings. 15-μm thick specimens were microtomed with a Leitz 1401 microtome and observed with an Olympus BH2 polarized light microscope.

Distribution and exfoliation level of clay was evaluated by TEM and XRD. XRD analysis was performed on pieces surface using a Phillips X’PERT MPD diffractometer (CuKα radiation λ=1.5418 Å, generator voltage=40 kV, current=40 mA). Measurements were recorded every 0.02 θ for 1 s each varying 2 h from 2 θ to 40 θ. The interlayer distance of clay was calculated from the (001) peak using the Bragg equation. TEM microphotographs were obtained with a TEM Jeol 100 CX microscope using an acceleration voltage of 200 kV. Samples were ultramicrotomed at room temperature with a diamond knife to a 70 nm-thick section.

Impact tests

The impact properties at room temperature of the mouldings were assessed by means of tensile (in-plane) and biaxial (out-of-plane) tests.

Tensile-impact tests were carried out at room temperature using a pendulum Ceast 6545 of 7.5 J. For these tests, rectangular samples were cut with a G-WEIKE LG900 laser engraver at different locations in the moulding: along the region of weld line formation at different melt collision angle (WL1 180º, WL2 140º, and WL3 110º); and away from the weld line, in a radial position along the flow direction (WWL), as shown in Fig. 2a. A 2 mm hole was drilled at the centre of the samples. The toughness, or tensile impact resistance, of the samples in the tensile test (J/m^2) was measured by the ratio between the fracture energy (J) and the broken surface area (m^2).

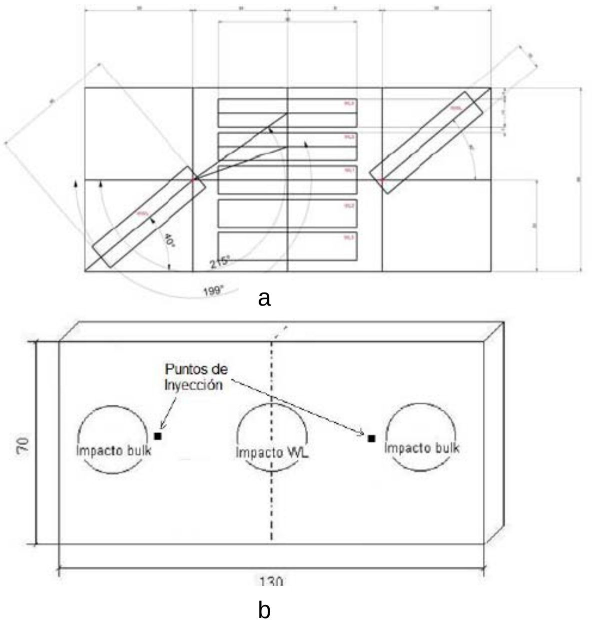

Figure 2 – Layout of tensile (a) and disc (b) test specimens.

Biaxial impact tests (with loading perpendicular to the plane containing one of the injection points) were carried out according to ASTM D 3763-93 in two locations of the pieces (on (WL) and out (bulk) of weld line) (Fig. 2b) using a Ceast Fractovis 6787 falling weight equipment. This equipment allows the load on the specimen to be continuously recorded as a function of time prior to fracture. This gives a more complete description of an impact than a single calculated value. The specimens were clamped between two steel plates with a circular opening of 40 mm in diameter. A velocity at impact of 1 m.s^{-1} was used. This technique is widely accepted for the out-of-plane fracture response assessment of polymeric composites because it gives a realistic view of in-service impact situations, hence being closer to real life conditions (Cunha et al, 1992; Bucknall, 2000). Moreover, it was found that this type of test was sensible to variation in skin-core structure induced by variations in processing settings (Cunha et al, 1992; Karger-Kocsis et al, 1999).

Results and Discussion

Microstructure of mouldings

The typical skin-core structure was found in mouldings (Fig. 3). Near the cold mould surface a frozen layer is formed adjacent to a shish-kebab or row structure developed, probably, in the region of highest shear rate.

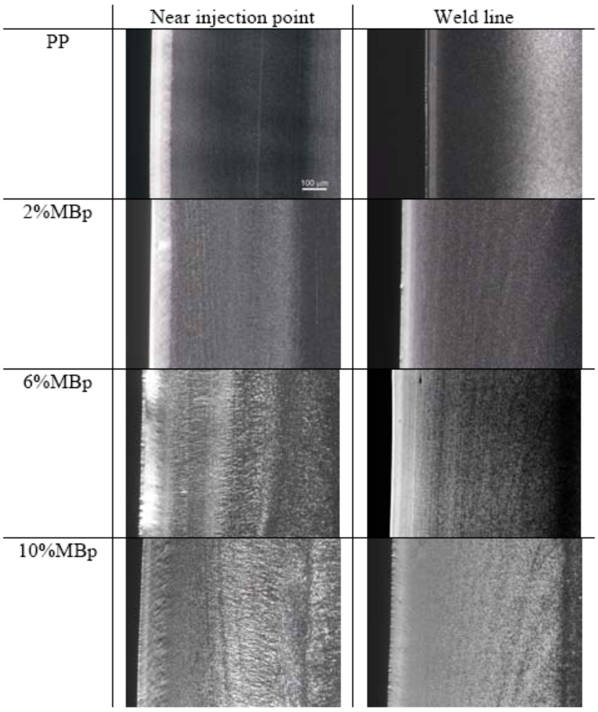

Figure 3 – Morphology of PP/nanoclay pieces injected according to experiment 2 (Table 2) observed by polarized light microscopy.

The shish-kebab structure is common in PP and other polyolefins and is a consequence of the fast crystallization of the polymer chains under high stresses near the skin region, as described by Fujiyama et al. (1988). In the vicinity of this sheared layer, β-spherulites can be found as a result of the crystallization under shear. In the core α-spherulites are formed under quiescent crystallization conditions. It is possible to observe the decrease of the skin thickness with the increase in MBp content (Fig. 4). This may be due to the nucleating effect of the nanoclay on PP. The distance from the injection points also influence the morphology. Thus, a reduction in skin thickness of samples on weld lines, away from the injection gates, when compared with samples near injection point could be verified (Fig. 4).

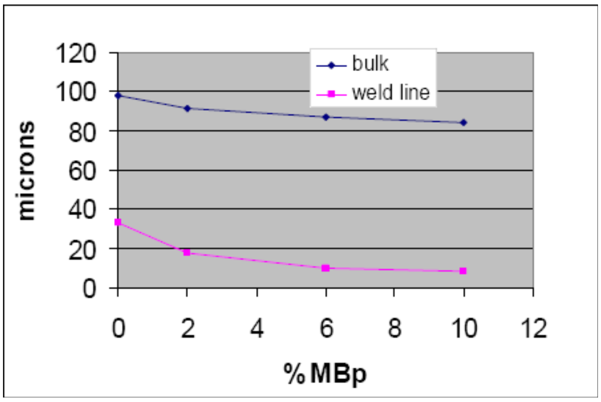

Figure 4 – Skin thickness of PP/nanoclay pieces injected according to experiment #2 (Table 2).

XRD confirmed the α nucleated effect of clay (Fig 5). Besides the main α−form crystallites (peaks at 2θ = 14.2, 17, 18.8 y 25.5º, corresponding to (110), (040), (130) and (131) planes), a small amount of β-form (peaks at 2θ = 16.2 y 21.2º, associated with (300) and (301) planes) was found in the skin layer of PP mouldings. This result is in agreement with other results reported in the literature (Kalay and Bevis, 1997). When clay was added to mouldings, intensities of peaks at 16.2º and 21.2º (β polymorph) diminished, while intensities of peaks at 17° and 25.5º (α polymorph) increased. It has been suggested that clay platelets have a similar effect as quenching, that is, they limit chain mobility (Fornes and Paul, 2003). This may be the cause of the decrease of β-form content in skin mouldings with increasing clay content.

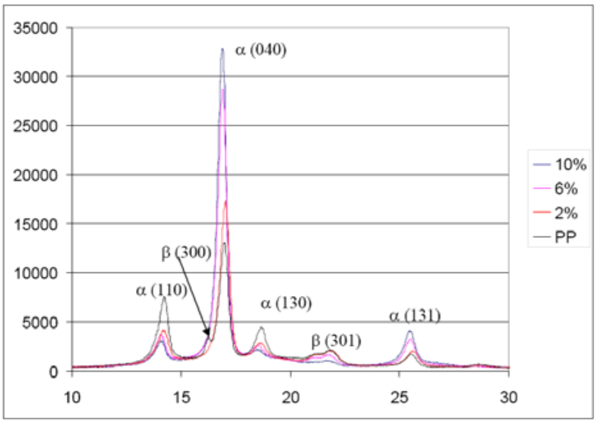

Figure 5 – XRD patterns (high 2θ) of PP/nanoclay pieces injected according to experiment 2 (Table 2).

Regarding clay exfoliation, XRD patterns indicated that clay platelets are only intercalated (Fig. 6), while in TEM pictures clusters of stacked sheets are clearly seen (Fig. 7). This is because the degree of clay dispersion not only depends on the affinity and compatibility of the organoclay with the matrix (which is an intrinsic factor dependent on the materials), but also on the shear stress (which is an extrinsic factor dependent on processing conditions and clay loading) (Dennis et al, 2001). Hence, the fact that, in our case, organoclay exfoliation is not complete is in part because the imposed processing conditions do not generate a shear force in the mix strong enough to delaminate completely the clay agglomerates.

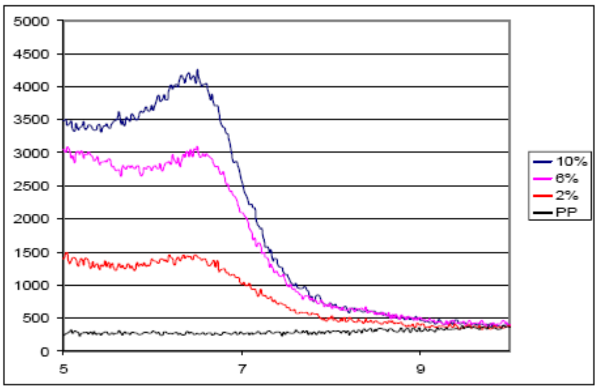

Figure 6 – XRD patterns (low 2θ) of PP/nanoclay pieces injected according to experiment 2 (Table 2).

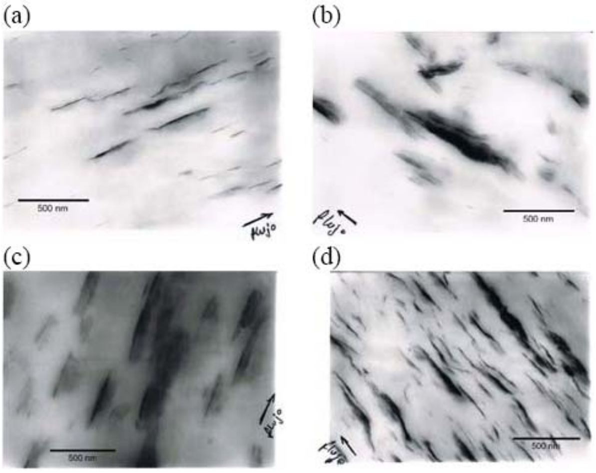

Figure 7 – TEM pictures of some PP/nanoclay pieces (a) 2% MBp (b) 6% MBp (c) 10% MBp (d) 14% MBp.

Influence of processing conditions on impact toughness

Figure 8 illustrates the effect of processing factors on the tensile and biaxial impact toughness following an ANOVA analysis (Keppel and Zedeck, 1989). The results show that MBp is the most influencing parameter, and impact toughness is practically not affected by the other processing conditions as reported before for other composites by Koster (1999) and Martinez Gamba et al (2009).

Pressure measurements inside the mould cavity go with this result (Fig. 9). Melt viscosity increased with clay content, inducing smaller pressures inside mould cavity. However, differences in pressure curves due to different clay content were not significant, indicating that clay did not affect processing conditions of boxes and changes in their mechanical properties are mainly due to MBp content.

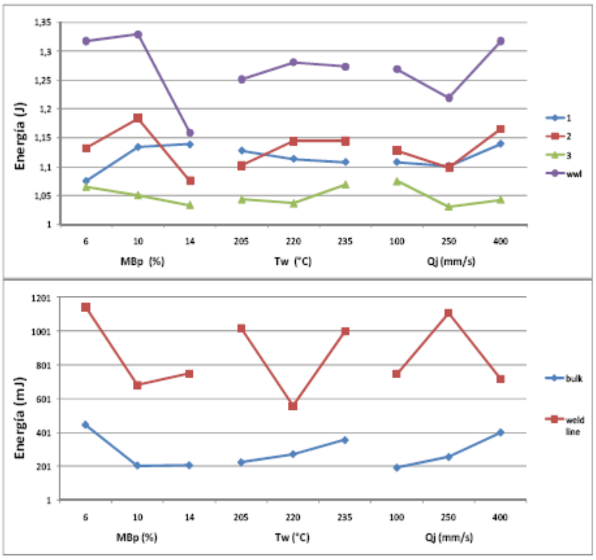

Figure 8 – Effects of processing parameters on impact toughness under (a) tensile impact and (b) biaxial impact.

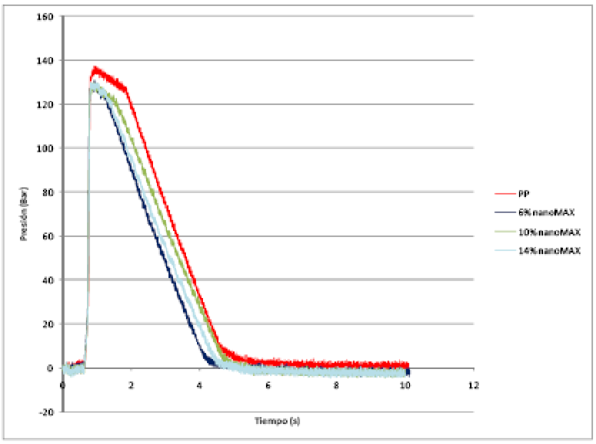

Figure 9 – Effects of clay content on pressure developed inside mold cavity.

Influence of the weld line on impact toughness

As expected, at the weld line the amount of consumed energy is lower than at the bulk under tensile conditions (Fig. 10).

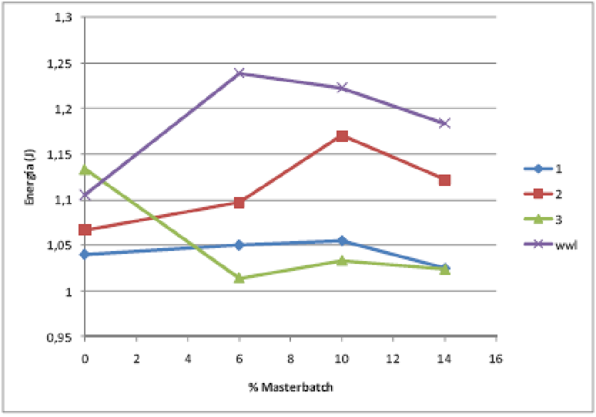

Figure 10 – Tensile impact toughness as a function of position in box and clay content.

It is possible to verify that the impact resistance tends to increase from a minimum associated to the sample WL1, where there is a frontal meeting of the flow fronts, to WWL, the reference sample in a location well away from the weld line in the flux direction. This trend may result both from geometrical aspects of the part and from the filling process of the moulding. It is useful to recall here the orientation of polymer molecules and clay platelets in the mouldings (Fig. 11).

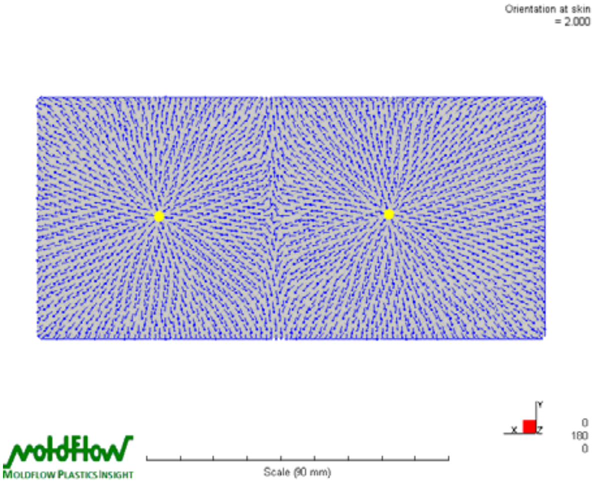

Figure 11 – Orientation of polymer molecules and clay particles as assessed by Moldflow.

It can be observed that the inclination of the weld line plane with respect to the specimen axis varies from a maximum of 90° (sample WL1) to a minimum around 45° (sample WL3). Therefore, at the region WL1, the polymer chains and the clay platelets are oriented in a plane transversal to the applied force, thus contributing to the weakness of this sample. In the other regions (WL2 and WL3), the weld line formed is not exactly perpendicular to the imposed tensile stress, which attenuates the depreciative effect of the weld line. The samples at location WWL show the best performance because of the absence of the weld line and the solicitation made in the flux direction.

A surprising result was that in PP mouldings weld line zone exhibited a more ductile behaviour (Fig. 12) and higher apparent impact toughness than the bulk under biaxial conditions (Fig. 13). The same result was previously reported by others (Bucknall, 1986). Visual inspection of biaxially impacted samples confirmed a larger fracture surface involved in the fracture of WL specimens (Fig. 14). Forming a larger fracture surface requires higher energy absorption. The macroscopic analysis of the fractured surfaces shown in Fig. 14 provides additional insight of the differences in the mechanical behaviour. This test does not impose a preferential direction of failure specimen. Consistently, isotropic or orthotropic materials are expected to display a symmetric deformation pattern to the impact site. The failures originate at the weakest point in the sample and propagate from there due to the high radial and circumferential tensile stresses (Alcock et al, 2006). The images show that the fracture patterns are

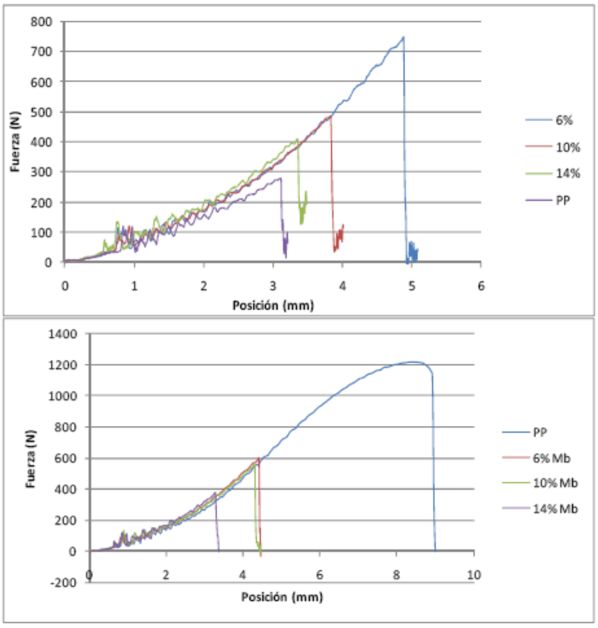

Figure 12 – Force-deflection curves recorded under biaxial impact in (a) bulk and (b) weld line zones.

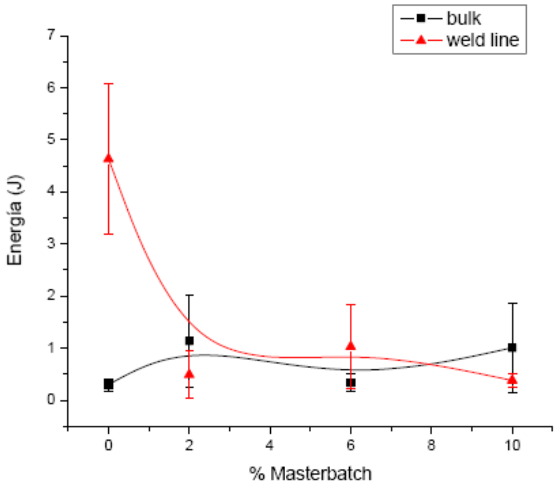

Figure 13 – Impact toughness of PP mouldings under biaxial loading.

significantly different. At the bulk of PP mouldings bending along the clamping ring becomes obvious. The plate failed by single splitting along the melt flow direction. Conversely, at the weld lines it can be seen that some cracks run radially from the central point of impact, while others follow a circular path around the same point (circular cracks occur where the depression caused by the striker produces a large bending moment and a high level of out-of-plane curvature), and there are evidence of plastic deformation (whitened zones). Therefore it is clear that the molecular orientation induced by melt flow prevailed, and the weld line were not the determinant of the toughness of the mouldings. On the other hand, weld lines of PP/nanoclay mouldings did not exhibit higher impact toughness than respective bulks. It is clearly seen that there is not only a main crack path along the melt flow direction in bulk samples, but also a main crack path along the weld line in weld line samples (Fig. 14).

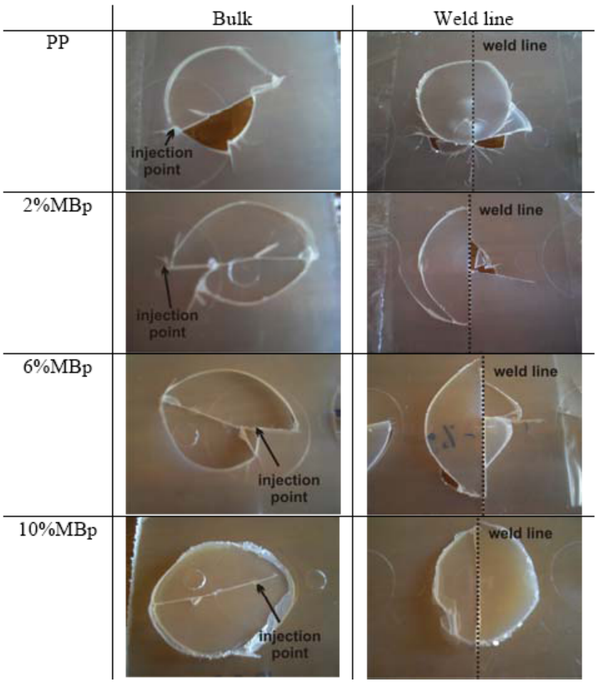

Figure 14 – Perforation patterns of mouldings.

This result is a consequence of lower molecular mobility and chain entanglement in the weld line, because of the viscosity increment resulting from the clay addition, and unfavourable orientation of the clay particles in the weld line plane. However, there is not a depreciation of impact toughness due to weld line formation, indicating that in these mouldings the molecular and particles orientation is the determinant of the toughness of the mouldings under biaxial loading, and not the weld line.

Influence of clay content on impact toughness

In the case of tensile tests, the lower values of the relationship between toughness at weld line and toughness at bulk were found with the sample WL1 (transversal plane of weld line), thus indicating the worse detrimental effect of the weld line in the tensile-impact resistance when it is perpendicular to the impact direction. This finding is a consequence of the orientation of the clay particles in the plane of the weld line, unfavourable to the direction of mechanical loading, and the higher melt viscosity of the composites with clay that decreases the molecular mobility, the chain entanglement, and the healing of the weld line. In biaxial tests, differences in perforation energy with clay content are negligible.

Analyzing all impact results, an optimum in impact performance was observed for mouldings with 6% of MBp (corresponding to 3% of nanoclay). It seems that at higher clay contents, clay platelets agglomerated and acted as defects, concentrating stresses.

Conclusions

In this work the uniaxial and biaxial impact response of injected PP/nanoclay mouldings was assessed.

The typical skin-core structure developed in the mouldings. A reduction of the skin with the increase in MBp content was observed probably due to the nucleating effect of clay on PP, also confirmed by XRD patterns. Besides a reduction in skin thickness of samples at the weld lines, away from the injection gates, when compared with samples near injection point was verified.

XRD and TEM analysis of mouldings showed that clay particles are at the most intercalated, indicating that the imposed processing conditions do not generate a shear force in the mix strong enough to delaminate completely the clay agglomerates.

ANOVA analysis revealed that the impact performance of the mouldings was practically not affected by the processing conditions (Tm and Qj), being MBp the most influencing parameter, which suggests that the matrix morphology may be not the leading factor in this type of materials.

Weld line zone of mouldings consumed less energy to fracture under tensile conditions than bulk zone due to molecular and clay orientation: in weld line the polymer chains and the clay platelets are oriented in a plane transversal to the applied force, while in the bulk molecules and clay platelets are oriented in the direction of the applied force.

Weld line zone of PP mouldings exhibited a more ductile behaviour and higher apparent impact toughness than bulk zone under biaxial conditions. Visual inspection of impacted samples showed that the molecular orientation induced by melt flow prevailed, and the weld line was not the determinant of the toughness of the mouldings. Differences between perforation energies of PP/nanoclay mouldings on bulk zones and weld line zones were negligible. Both main crack paths along the melt flow direction and along the weld line were seen, due to the lower molecular mobility and chain entanglement in the weld line, (because of the viscosity increment resulting from the clay addition) and unfavourable orientation of the clay particles in the weld line plane. In summary, in these mouldings the molecular and particles orientation was the determinant of the perforation energy, and not the weld line.

An optimum in impact performance was found for mouldings with 6% of MBp (corresponding to 3% of nanoclay). It seems that at higher clay contents, clay platelets agglomerated and acted as defects, concentrating stresses.

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