Microstructure of PP/clay nanocomposites produced by shear induced injection moulding

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Abstract

The maximum property enhancement in nanoclays reinforced polymers is obtained when high levels of intercalation, exfoliation and dispersion of the nanoclay in the polymer matrix is achieved. Processing of polymer nanocomposites by melt blending techniques requires sufficient stress levels and time for a maximum exfoliation/intercalation of the nanoclays (with minimum polymer degradation), which both are very limited in conventional polymer processing techniques. Shear Controlled Orientation in Injection Moulding, SCORIM, is a non-conventional injection moulding technique based on the concept of in-mould shear manipulation of the melt during the polymer solidification phase. This technique is able of applying high shearing levels to the polymer, leading to high levels of molecular orientation. SCORIM of nanoclay-based polymer nanocomposites may be therefore beneficial for achieving high levels of nanoclay intercalation/exfoliation and orientation, thus imparting improved mechanical properties. In this work, a nanoclay based masterbatch was mixed with polypropylene and direct injection moulded by conventional and SCORIM techniques. In SCORIM, two extreme shear levels were applied by changing processing conditions (melt temperature and shear time). We assess therefore the effect of high shear conditions in the levels of intercalation/exfoliation and orientation of the nanoclay in the polymer matrix and in the mechanical properties of the nanocomposite. The levels of clay intercalation/exfoliation were evaluated by Wide-Angle X-ray Scattering. The microstructure of the moulding was characterized by X-ray diffraction, polarized light microscopy and DSC. Besides influencing the nanoclay morphology, a

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strong coupling with the polymer morphology is also observed, evidencing the nanoclays as polymer morphology
directors.

Keywords: polypropylene; nanocomposites; injection molding; SCORIM

1. Introduction

The possibility of manufacturing nano-composites from melt-mix polymers with layered silicates, without
the use of organic solvents with tailored properties at low cost has gained much interest. (Frontini and
Pouzada, 2011; Ray and Okamoto, 2003; Vaia et al, 1993). Particular interest has been paid to clay
 nanoplatelets and their composites with non-polar thermoplastic polyolefin matrices, namely polypropylene
(PP) in the last two decades (Alexandre and Dubois, 2000; Manias et al, 2001; Paul and Robeson, 2008).
Potential areas for practical applications include mechanical performance and toughness improvement, surface
hardening, fire retardancy, or, solvent permeability reduction.

The mechanical and physical properties of these composites arise not just from the combination of
compounds, but also from the morphologies developed. It is stated that the performance quality of
nanocomposites is intimate related to the degree of dispersion: only well-dispersed and well-exfoliated
nanoparticles can lead to the expected improvement of properties (Bousmina, 2006; Paul and Robeson, 2008).
Unfortunately, the degree of clay exfoliation 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).

Achieving a proper dispersion level of PP/ nanoclay composites processed by conventional injection
moulding (CIM) constitutes a difficult challenge task (Rajesh et al, 2012), since the imposed processing
conditions do not generate a shear force in the mix strong enough to delaminate completely the clay
agglomerates (Pettarin et al, 2011; Pettarin et al 2012). Besides, the presence of voids and defects in thick
specimens is a common feature in moldings obtained using industry achievable processing conditions.

Non convention Injection molding like the so-called shear-controlled orientation in injection molding
(SCORIM) process offers potential benefits through controlling the microstructure of moulded materials. The
main difference of these non-conventional melt manipulation injection moulding processes in comparison to
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 (Kikuchi et al, 2002; Bilewicz et al, 2006; Bilewicz et al, 2007;
Bilewicz1 et al, 2008; Bilewicz2 et al, 2008).

This paper shows the differences in microstructures developed during the moulding process of thick
PP/nanoclay parts using both CIM and SCORIM as injection molding process. Microstructure is analyzed by
polarized light microscopy, differential scanning calorimetry and X-ray diffraction. In order to investigate the
most significant injection molding parameters for SCORIM, ANOVA analysis is applied.
2. Experimental

2.1. Materials and processing

The materials used in this work are shown in the Table 1. Ratios of particular materials, which composites are composed of, are listed in the Table 2.

All compositions were injection molded into rectangular bar specimens with dimensions of 130x13x8 mm, by using Ferromatik Milacron injection-molding machine type K-85A, equipped with a special mounted SCORIM mold with manifold and hydraulic system.

The SCORIM molding programme was defined according to a design of experiments (DOE) approach. Based on the 3-factorial, 3-level array, experiments followed the 9-run table (Table 3), which contains 3 values for each changeable processing parameter. It has been done to include terminal mechanical behaviors of composites. Three changeable processing parameters were considered in the molding programme: the melt temperature, stroke time (responsible for time of piston movements) and stroke number (number of piston movements). Injection pressure, exerted by screw into the cavity, as well as other parameters, was kept constant (Table 4). The materials were previously blended in a rotative drum at the speed of 60 rpm.

For comparison purposes CIM samples were injected according to Table 4 with a melt temperature of 200°C. This condition was selected from simulations performed using Moldex3D adopting as optimum rheological parameters the ones emerging from our own experience (Pettarin et al, 2012).

Table 1. Materials used in the experiments

| Homopolymer polypropylene (PP) | Domolen 1100L |
|--------------------------------|---------------|
| Nanoclay Masterbatch (50%PP/50%Nanoclay) | P-802 Nanocor |

Table 2. Particular components (wt%)

| Abbreviation | PP | MB |
|--------------|----|----|
| PP           | 100| 0  |
| PP/MB-1      | 97 | 3  |
| PP/MB-2      | 95 | 5  |
| PP/MB-3      | 93 | 7  |

Table 3. Variable injection processing set-up for SCORIM

| Run | Stroke time (s) | Melt temperature (°C) | Stroke number |
|-----|----------------|-----------------------|---------------|
| 1   | 1              | 200                   | 3             |
| 2   | 1              | 220                   | 7             |
| 3   | 1              | 240                   | 13            |
| 4   | 2              | 220                   | 13            |
| 5   | 2              | 240                   | 3             |
| 6   | 2              | 200                   | 7             |
| 7   | 3              | 240                   | 7             |
| 8   | 3              | 200                   | 13            |
| 9   | 3              | 220                   | 3             |
2.2. Characterization

Polarized light microscopy (PLM) was used to observe the microstructure of the mouldings. 15µm thick samples were cut with a Leitz 1401 microtome and observed with an Olympus BH2 polarized light microscope.

The global crystallinity of the mouldings was determined after differential scanning calorimetry (DSC) tests on specimens with the whole skin-core structure using a Perkin-Elmer equipment at a heating rate of 10ºC/min. The crystallinity was calculated as:

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

where $\Delta H$ is the apparent enthalpy of fusion per gram of composite, $\Delta H^0$ is the heat of fusion of a 100% crystalline PP which is of 207.1 kJ/kg (Brandrup et al, 1999), and $\phi$ is the weight fraction of MB in the composites.

XRD analysis was performed on samples from the skin layer using a Phillips XPERT MPD diffractometer (CuKα radiation $\lambda=1.5418\AA$, generator voltage=40kV, current=40mA). Measurements were recorded every 0.02° steps for 1s, each varying 2θ from 2 to 40°. The interlayer distance of the nanoclay was calculated from the (001) peak using the Bragg’s law ($\lambda = 2d_{001}\sin\theta_{001}$). The analysis was performed on samples surface (skin) and on a transversal cut of the samples (core) as shown in figure 1.

From the wide angle X-ray diffraction (WAXD) pattern, the PP α-phase orientation indices were determined as (Trotignon et al, 1982):

$$A_{110} = \frac{I_{110}}{I_{110} + I_{111} + I_{131+041}}$$

$$C_\alpha = \frac{I_{040}}{I_{110} + I_{040} + I_{130}}$$

where $I$ is the peak height after background subtraction, $\alpha_1$ corresponds to the (110) reflection, $\alpha_2$ to the (040) reflection, $\alpha_3$ to (130) reflection and $\alpha_4$ to the (111) and (041) reflections. The $A_{110}$ index is based on
the extinction of (hk0) reflections relatively to the (0k0) reflections and gives an indication of a preferential orientation perpendicular to the b-axis, i.e. pretty much parallel to the surface sample (Zhu and Edward, 2003).

3. Results and discussion

Fig. 2 is representative of the cross sections of the mouldings as observed by PLM. Visible difference between CIM and SCORIM morphology is the shrinkage of CIM specimens. Avoiding this shrinkage was achieved when SCORIM technique was used. In the case of PP/nanocomposites injected by CIM internal voids are clearly seen. The use of SCORIM helps to avoid the formation of these voids.

Neat PP evidences structure development and complete rectangular shape achieving after use of SCORIM. Main difference between techniques can be observed from the photographic matching. The skin/core structure for conventionally injected specimens and the typical layered structure of melt manipulation technique are clearly seen. The SCORIM samples feature a thick shear zone, which contains many oriented layers.

Addition of nanoclay diversified the morphology, especially developing the shear zone into a thicker multilayer zone. Similar findings were previously reported (Bilewicz M. et al, 2008; Dobrzanski et al, 2008). Also an increase of the skin thickness with the increase in MB content was observed (fig. 3). The ANOVA analysis indicates that PP/nanoclay composites are more sensitive than neat PP to processing settings (fig 4). It was found that high shear rate induced a thicker skin, while high temperature induced a thinner skin.

![Fig. 2. Typical polarized light micrographs of PP composites](image)
Fig. 3. Skin thickness of neat PP and PP/nanoclay composites obtained by SCORIM.

Fig. 4. ANOVA analysis of results shown in figure 3.

DSC results showed that the amount of overall crystallinity of SCORIM PP mouldings increased with the addition of nanoclay (Fig 5). The ANOVA analysis indicates that both high shear rate and high temperature induced a high degree of crystallinity (Fig 6).

Typical XRD patterns are shown in figure 7. In neat PP differences between samples obtained by CIM and SCORIM are minimal. Also skin and core reflections are similar, indicating similar crystal morphologies and orientation. In the case of SCORIM, the amorphous halo is larger in the skin than in the core.

Fig. 5. Crystallinity of neat PP and PP/nanoclay composites molded by SCORIM as assessed by DSC.
Fig. 6. ANOVA analysis of results shown in figure 5.

| Factor level | Stroke Time | Stroke Number | Melt Temperature |
|--------------|-------------|---------------|------------------|
| PP           | PP + nano   | PP + nano     | PP + nano        |

| % crystallinity | 25 | 30 | 35 | 40 | 45 | 50 |
|-----------------|----|----|----|----|----|----|
| PP              | 15 | 17 | 19 | 21 | 23 | 25 |
| PP + nano       | 12 | 14 | 16 | 18 | 20 | 22 |

Fig. 7. Typical XRD patterns of PP composites

CIM

SCORIM

Neat PP

PP + 3% nanoclay
The presence of nanoclay induced changes in the crystal structure of PP. The conventional moldings exhibit a low β-phase content, the intensities of β-phase reflection from the SCORIM moldings is very low in comparison to the CIM moldings. The doublet (111)-(041) is smaller in X-ray spectra of SCORIM samples. This diminishment indicates a higher orientation of PP molecules in SCORIM samples (Kalay and Bevis, 1997), since the monoclinic α phase of PP has an epitaxial relationship to the γ phase of PP such that each can grow on the lamella of the other. Marked differences in crystalline structure at the core and the surface of injected nanocomposites were observed, being more intense in the case of SCORIM pieces. Three PP polymorphs, α, β and γ, were detected in the core while only α and γ polymorphs were detected in the skin. A γ phase dominance is seen in the higher intensity of the 17° peak relative to the 14° peak in the skin. The doublet (111)-(041) is smaller in the skin than in the core, indicating a higher orientation of PP molecules in skin. It seems that there are no differences in the amount or orientation of PP crystals in the core of PP/nanoclay and neat PP. However, in the X-ray spectra of the skin of PP/nanoclay the intensities of peaks at 16.2° and 21.2° (β polymorph) were attenuated, while the intensity peaks at 17° and 25.5° (α polymorph) were enhanced. Nanoclay acted as α nucleation site, reducing the amount of β-form PP. Another important feature is the increase of the (040)/(110) ratio. Orientation indexes indicate that in SCORIM pieces nanoclay induced the orientation of the crystalline-phase of PP in the (040) direction – i.e. increase of degree of epitaxiality (Kim et al, 2004) – and a low level of crystalline phase orientation in the flow direction (fig 8). Regarding processing conditions, it was found that the variations of A_{110} and C_{α} are small (especially the latter), A_{110} increases with shearing and C_{α} decreases with melt temperature (fig 9).

Regarding nanoclay exfoliation in both CIM and SCORIM, in the X-ray spectra of nanocomposites skin the peak corresponding to the (001) interlayer basal spacing of the nanoclay can be clearly seen (fig 7), illustrating the intercalation of polymer between the galleries of clay layers with an intergallery space of 13.4 nm for all systems. On the other side, the absence of the (001) peak in the X-ray spectra of nanocomposites core indicate an exfoliated structure (fig 7). Other authors have previously reported similar findings (Hernandez-Luna, 2003). They stated that the addition of nanoclay plus maleic anhydride PP (mPP) produces in the PP a dual effect. First, the nanoclay tends to emigrate to the surface of the specimens, pulled by the maleic anhydride. This could be thought as an effect contrary to what is desired. However, the viscosity of the systems does not allow the complete emigration of the fillers. As consequence of this emigration effect and being the nanoclay and mPP bond to each other, the nanoclay is better exfoliated in the matrix, pulled by the mPP in its way to the surface.
4. Conclusions

Trough this work the microstructre of PP/nanoclay pieces obtained by a non-conventional injection molding technique like the so-called shear-controlled orientation in injection molding (SCORIM) is studied. We found that incorporation of nanoclay changes the developed morphology. Adding nanoclay to PP results in low level of crystalline phase orientation in the flow direction and Increment upon the degree of epitaxiality. Clay also act as α phase nucleating agent also diminishing β phase and increasing epitaxiality. Both skin layers thickness and degree of crystallinity of the skin layer increase with the percentage of incorporation of nanoclay. High shear levels lead to thicker skin; high thermal levels to thinner skin. Adding nanoclay results in a moderate increment upon the overall degree of crystallinity. High shear and thermal levels lead to a higher overall degree of crystallinity. When compared with conventional injection molding, SCORIM results in a higher degree of crystallinity of the skin layer.

In summary, it was found that for PP, a semicrystalline polymer, nanoclay acts as morphology directors, and the concomitant use of SCORIM and nanoclays results in distinct morphologies. It is expected that this changes will be reflected in the mechanical properties of the mouldings. Further work is in progress to understand the influenced of the induced morphology upon fractue behavior.

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References

Alexandre M., Dubois P., 2000, Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials, Materials Science and Engineering 28, 1-63

Bilewicz M., Viana J.C., Cunha A.M., Dobrzański L.A., 2006, Morphology diversity and mechanical response of injection moulded polymer nanocomposites and polymer-polymer composites, Journal of Achievements in Materials and Manufacturing Engineering 15, 159-165

Bilewicz M., Viana J.C., Dobrzański L.A., 2007, Self reinforced polymer-polymer composites, Journal of Achievements in Materials and Manufacturing Engineering 2, 43-46

Bilewicz M.1, Viana J.C., Dobrzański L.A., 2008, Development of microstructure affected by in-mould manipulation in polymer composites and nanocomposites, Journal of Achievements in Materials and Manufacturing Engineering 31, 71-76

Bilewicz M.2, Viana J.C., Dobrzański L.A., 2008, Polymer composite strengthening by developed injection moulding technique, Archives of Materials Science and Engineering 30, 69-72

Brandrup, J., E. H. Immergut, et al., 1999, Polymer Handbook. Wiley, New York

Bousmina M., 2006, Study of Intercalation and Exfoliation Processes in Polymer Nanocomposites, Macromolecules 39, 4259-4263

Dennis H.R., Hunter D.L., Chang D., Kim S., White J.L., Choc J.W., Paul D.R., 2001, Effect of melt processing conditions on the extent of exfoliation in organoclay-based nanocomposites, Polymer 42, 9513–22

Dobrzański L.A., Król M., Bilewicz M., Viana J.C., 2008, Microstructure and mechanical properties of Polypropylene/Polycarbonate blends, Journal of Achievements in Materials and Manufacturing Engineering 27, 19-22

Frontini P. M., Pouzada A. S., 2011, Is there any chance for polypropylene/clay nanocomposites in injection molding?, Express Polymer Letters 5(8), 661-661

Hernandez-Luna A., 2003, Structure property and deformation analysis of polypropylene montmorillonite nanocomposites; PhD Thesis, University of North Texas

Kalay G., Bevis M.J., 1997, Processing and Physical Property Relationships in Injection-molded Isotactic Polypropylene. 2. Morphology and Crystallinity, Journal of Polymer Science: Part B: Polymer Physics 35, 265–291

Kikuchi A., Coulter J.P., Angstadt D.C., 2002, Polymer Melt Manipulation and In-Process Morphology Control during Molding Processes: A Review - Journal of Injection Molding Technology 6(2), 91

Kim B., Lee S.-H., Lee D., Ha B., Park J., Char K., 2004, Crystallization Kinetics of Maleated Polypropylene/Clay Hybrids, Industrial & Engineering Chemistry Research 43, 6082-6089

Manias E., Touny A., Wu L., Strawhecker K., Lu B., and Chung T. C., 2001, Polypropylene/Montmorillonite Nanocomposites. Review of the Synthetic Routes and Materials Properties, Chem. Mater. 13, 3516-3523

Paul D.R., Robeson L.M., 2008, Polymer nanotechnology: Nanocomposites, Polymer 49, 3187-3204

Pettarin, V., Viau G., Fasce L., Viana J., Pontes A., Frontini P., Pouzada A., 2011, Impact behaviour of double-gated nanoclay-reinforced polypropylene injection mouldings, Polym. Eng. Sci. submitted

Pettarin, V., Brun F., Viana J., Pouzada A., Frontini P., 2012, Toughness distribution in complex PP/nanoclay injected mouldings, Composites Science & Technology, submitted

Rajesh J. J., Soulestin J., Lacrampe M. F., Krawczak P., 2012, Effect of injection molding parameters on nanofillers dispersion in masterbatch based PP-clay nanocomposites, eXPRESS Polymer Letters 6(3), 237–248

Ray S.S., Okamoto M., 2003, Polymer/layered silicate nanocomposites: a review from preparation to processing, Prog. Polym. Sci. 28, 1539–1641

Trotignon J.P., Lebrun J.L., Verdu J., 1982, Crystalline polymorphism and orientation in injection-moulded polypropylene, in: “Plastics and Rubber Processing and Applications”, Vol. 2, 247-251

Vai A.R., Ishii H., Giannelis EP., 1993, Synthesis and properties of two-dimensional nanostructures by direct intercalation of polymer melts in layered silicates, Chem Mater 5, 1694–1696

Zhu P.-W., Edward G., 2003, Studies of injection-moulded isotactic poly(propylene) by synchrotron WAXD/SAXS: Effects of nucleating agent on morphological distribution, Macromolecular Materials and Engineering. 288, 301-311