Surface property effects of compounding a nanoclay masterbatch in PP injection moulding

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ABSTRACT: The interest on the use of nanofillers in injection mouldings has been going on for more than a decade but a real breakthrough has not been achieved yet, especially in that mechanical properties are concerned. The nucleating effect of nanoclays in semicrystalline polymers suggests that surface effects may result interesting especially during processing. This paper includes some information on the surface properties of an injection moulding grade of polypropylene mixed with a commercial masterbatch of PP and 50% of organoclay. They were moulded as plates for testing in a prototype device for determining the coefficient of friction in as-moulding conditions. The surface was also characterised by depth sensing indentation tests. The through thickness microstructures of the mouldings were assessed by optical microscopy and differential scanning calorimetry, while surface morphology was assessed by X-ray diffraction. It was observed that independently of MB content, its addition caused a slight increase in elastic modulus and hardness in the skin layer.The friction properties directly associable to the product performance showed a slight improvement in terms of the dynamic friction coefficient. Conversely the static friction coefficient that is relevant in processing was no affected by the presence of the nanoclay.

1 INTRODUCTION

In the last decade nanocomposites based on thermoplastics modified with nanoclays turned up as a topic of industrial and academic interest. These nanocomposites have been reported to exhibit visible improvements when compared with the corresponding raw materials and micro and macro-composites (Reynaud et al. 1999). Simultaneously propylene polymers (homo and copolymers) -PP- are increasingly being used for industrial automotive applications due to their advantageous properties: broad portfolio, low density, environmental stress-cracking resistance, unique ability to form integral hinges, price and ability to be readily recycled, among many others. 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 (Karger-Kocsis 1993).

In order to improve the mechanical properties of thermoplastics, composites with various nanofillers have been tested, namely organic nanoclays (Zhang et al. 2004). However only well-dispersed and well-exfoliated nanoparticles can lead to the expected improvement of properties (Krawczak 2007). 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.

The nucleating effect of nanoclays in semicrystalline polymers suggests that surface effects may result interesting especially during processing. This paper includes some information on the surface properties of an injection moulding grade of polypropylene mixed with a commercial masterbatch of PP and 50% of organoclay.

2 EXPERIMENTAL

2.1 *Materials*

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

2.2 *Mouldings*

Nanocomposites were obtained by direct injection of mixtures of PP and MB. Various 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.

Figure 1. Injection mouldings. Colour varies with the percentage of MB content.

The nanocomposites were produced with masterbatch percentages of 2, 6, and 10%. The processing conditions, which were adjusted following a study presented elsewhere (Viau et al. 2009) are listed in Table 1.

Table 1 – Processing settings

Processing parameter	Unit	Value
Injection temperature	ºC	235
Injection pressure	MPa	5
Packing pressure	MPa	3
Injection time	S	1
Packing time	S	10
Cooling time	S	15

2.3 *Characterisation*

2.3.1 *Morphology*

The crystallinity of the moulded materials was determined after DSC tests on specimens with the whole skin-core structure using a Perkin-Elmer equipment at a heating rate of 10ºC/min. The crystallinity of PP matrix was calculated as:

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

where ΔH is the apparent enthalpy of fusion per gram of composite, ΔH^0 is the heat of fusion of a 100% crystalline PP, 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 polarized light microscope.

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 2θ from 5° to 40°.

2.3.2 *Depth sensing indentation*

Depth sensing indentation measurements were performed using a Triboindenter Hysitron equipped with MRNP device. Indentations were done with a Berkovich shaped diamond tip at two different conditions as shown in Figure 2 and described bellow:

i) in order to obtain the skin properties, indentations were performed onto the surface of the as molded pieces applying a trapezoidal load cycle up to 50mN, at a loading/unloading rate of 10mN/s and a dwell time of 20s.

ii) aiming to get the mean properties of the core region, indentations were performed through the thickness of the moldings. A smooth surface was prepared with a microtome under cryogenic conditions. The maximum load was 8mN, the loading/unloading rate was 0.5mN/s and a dwell time was 20s.

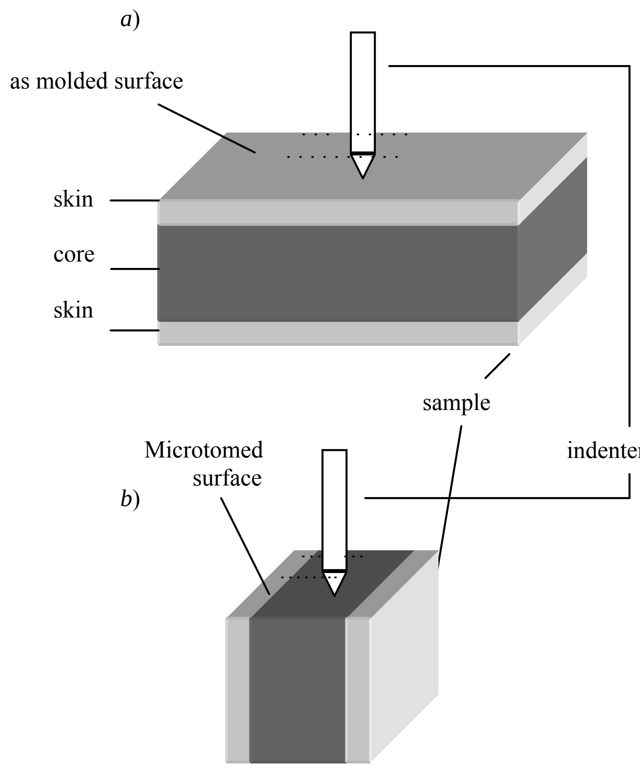

Figure 2. Scheme of samples used in depth sensing indentation experiments for determination of *a*) skin properties and *b*) core properties. Dots indicate indentation locations.

Indentation load-penetration depth data were analyzed in terms of the Oliver and Pharr approach (Oliver and Pharr 1992) to obtain reduced elastic modulus and hardness. Reported values are the average values of at least 50 indentations for each condition and material.

2.3.3 *Friction*

The friction properties of the moulded materials were determined against a surface whose roughness Ra was of 0,7 µm, as measured with a profilometer Phertometer M2. The coefficient of static friction was determined with a prototype apparatus using the experimental technique proposed by Pouzada *et al.* (Pouzada et al. 2006). A scheme of the test setup is shown in Figure 3.

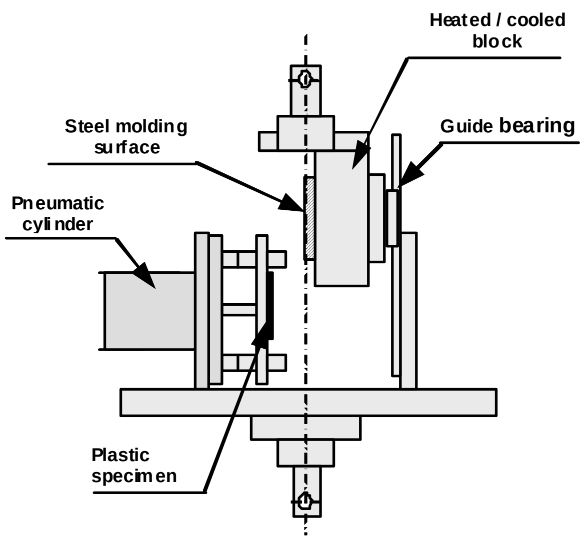

Figure 3. Scheme of the friction measurement apparatus (Pouzada et al. 2006).

Determination of the coefficient of friction was done without replication at 25ºC (for assessment of the friction properties of the surface in use) and with replication at 40°C (to observe the effect of the influence of the MB during the ejection of the moulding). The contact pressure was set at 600 kPa. The crosshead speed of the Instron machine where the device was mounted was of 100 mm.s^{-1}.

3 RESULTS AND DISCUSSION

3.1 *Morphology of mouldings*

Typical skin-core structure developed in moldings during processing as revealed by TOM and a decrease in the skin thickness with the increase in MB content was found (Figure 4). Also XRD patterns indicated differences in crystalline structure of skin layer, as intensities of peaks corresponding to α-PP phase change with clay content (Figure 5). As differences in surface morphology were induced by MB, differences in surface properties were expected. DSC traces of the various moulded materials are shown in Figure 6. The analysis of these tests showed that the amount of overall crystallinity did not vary significantly with the amount of MB.

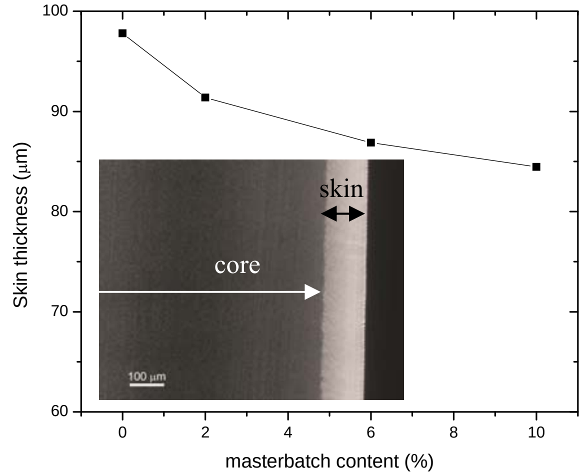

Figure 4. Optical microscopy results: typical skin-core structure seen in moldings and skin thickness near injection point as a function of masterbatch content.

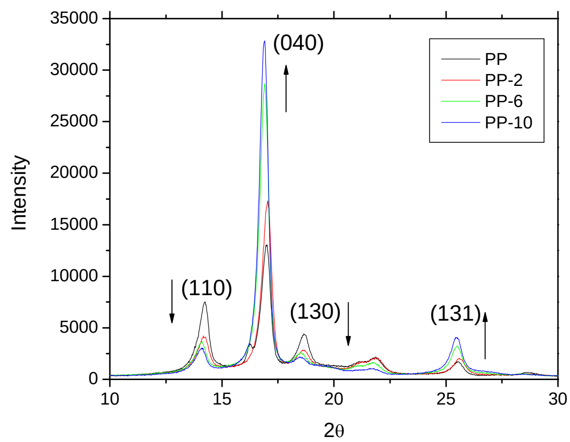

Figure 5. XRD patterns of PP/nanoclay pieces surfaces.

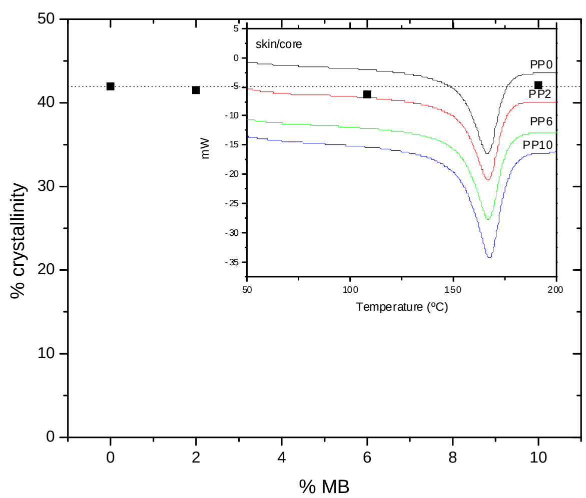

Figure 6. DSC results: percentage of crystallinity as a function of MB content among with DSC traces.

3.2 *Reduced Elastic Modulus and Hardness*

In the case of indentations performed at 50mN of maximum applied load, the penetration depth reached by the indenter was about 6 μm. This implies that the material involved under the indenter belongs to the skin layer of the moldings (see Figure 4). This verify that the properties of the skin could be evaluated from these experiments.
The indentation responses measured through the thickness varied with the relative location with respect to the molding edge, as shown in Figure 7 for one of the tested samples. Therefore, measurements in the edge zone were not taken into account to obtain the properties of the core region.

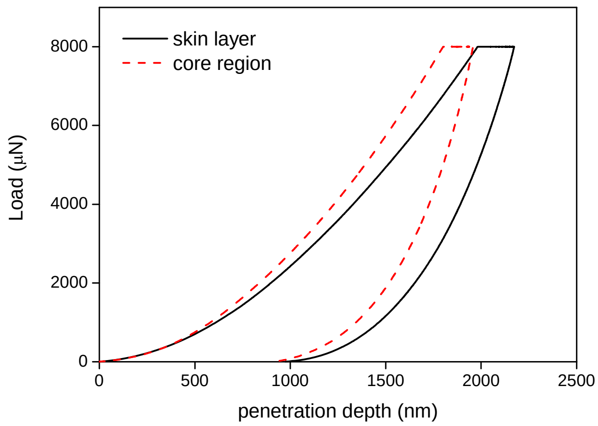

Figure 7. Typical indentation load-penetration depth curves obtained for PP-2 sample in experiments performed through the thickness of the molding.

Reduced Elastic Modulus and Hardness average values are plotted respectively in Figures 8 and 9 as a function of MB content in the moldings for the skin and core regions.

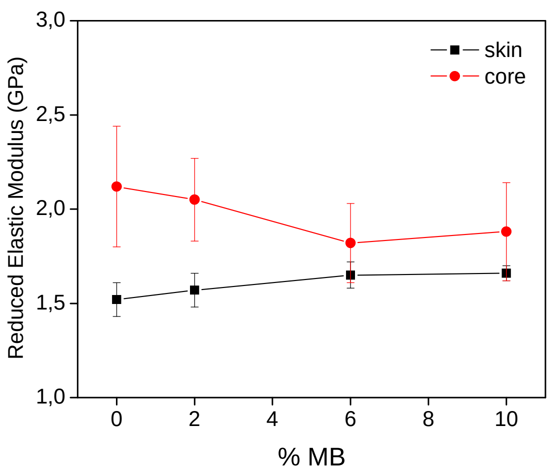

Figure 8. Comparison of Reduced Elastic Modulus values vs. masterbatch content in the skin and core regions of moldings.

In PP moldings the difference between properties in the skin layer and core region was very marked. The core region showed up to be stiffer and harder than the skin region. The incorporation of MB affected the properties of the skin and core regions dissimilarly. Independently of MB content, its addition caused a slight increase in elastic modulus and hardness in the skin layer. On the other hand, in the core region the presence of MB in amounts up to 6% generated a gradual reduction in elastic modulus and hardness. Larger MB content did not further affect properties. This can be explained by the combination of opposite effects of the MB in the composites: a stiffening reinforcement of the clay together with a plasticization action of PP-MAN.

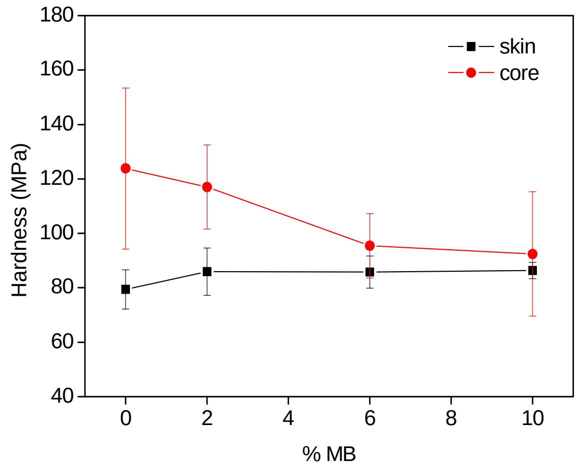

Figure 9. Comparison of Hardness values vs. masterbatch content in the skin layer and core regions of moldings.

These results suggest that the incorporation of 6% MB leads to a molding with slightly stiffer and harder surface and with less variation in through the thickness mechanical properties.

3.3 *Friction properties*

One may look at the friction behaviour under two points of view: the performance of the plastics products where the coefficient of friction determined by standard methods is appropriate; and the ejection of the moulding from the mould, where the replication effect must be taken into account.
The data in Figure 10, referring to tests without replication, shows that the composition of nanoclay does not lead to a noticeable change in the static coefficient of traction. On the contrary the coefficient of dynamic friction, shows a slight reduction. This may suggest that the addition of a small percentage of nanoclays may improve the performance of products with sliding performance as a specification. Even so the gain in using this somewhat expensive conclusion is not larger than 10%.
The test with replication at 40ºC, this might being a possible temperature of ejection of the mouldings, is not so discriminative about the usefulness of the nanoclay compounding. The influence of the amount of nanoclay in the polymer nanocomposite does not appear to have a meaningful influence on the static coefficient of friction under these circumstances.

As a matter of record the coefficient of friction is 0,24 without replication and 0,36 with replication in a moulding surface with Ra=0,7 µm.

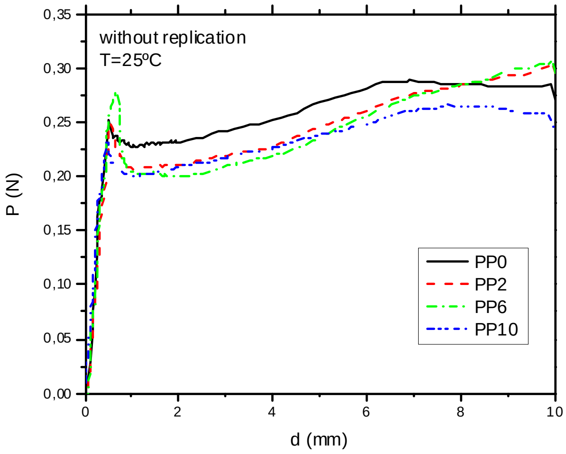

Figure 10. Friction tests at 25ºC without replication.

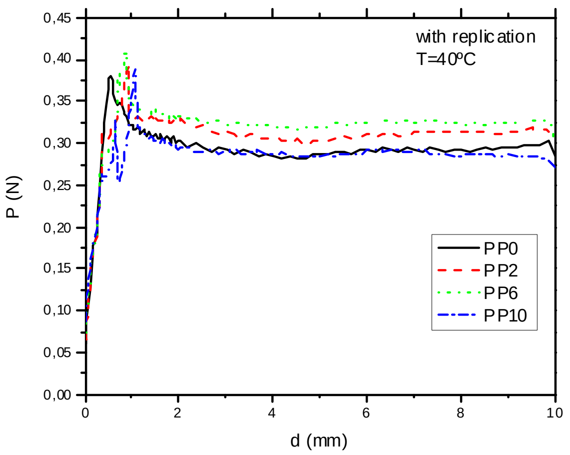

Figure 11. Friction tests at 40ºC with replication.

4 CONCLUSIONS

The studies on PP nanocomposites obtained in standard processing conditions using a commercial organoclay masterbatch with an injection moulding grade of PP were aimed at identifying performance gains resulting from friction effects of the nanocompounding.

Independently of MB content, its addition caused a slight increase in elastic modulus and hardness in the skin layer.

The friction properties directly associable to the product performance showed a slight improvement in terms of the dynamic friction coefficient. Conversely the static friction coefficient that is relevant in processing was no affected by the presence of the nanoclay.

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