Synergistic effects of nanoclay and SGF on tribological and dynamic properties of polypropylene composites

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Abstract. In recent year's polymer/layered silicate (PLS) nanocomposites have attracted great interest, both in industry and in academia, because they often exhibit remarkable improvement in materials properties when compared with virgin polymer or conventional micro and macro-composites. These improvements can include high moduli, increased strength and heat resistance, decreased gas permeability and flammability, and increased biodegradability of biodegradable polymers. However these properties are strongly influenced by how the clay is dispersed in the polymer.

In this study the synergistic effects in PP+short glass fiber+nanoclay systems in the tribogical and dynamic properties in injection mouldings were analysed.

The materials used were a Polypropylene Homopolymer, Nanoclay (montmorillonite layer silicate) for Polyolefin Nanocomposites in percentages of 2%, 6% and 10% and a Polypropylene Homopolymer with content of 10% and 30% of glass fiber reinforced.

The various materials systems were characterized in terms of dynamic properties and tribological properties. Several tests were conducted which includes the measurements of coefficient of friction in conditions similar to the ejection phase in injection moulding process. The microstructure of the mouldings was characterized by DSC.

Polymer properties are determined by the incorporation of nanoclays, SGF and by processing. Moreover influencing the microstructure of the mouldings and a synergistic effect of the nano and micro reinforcements are also observed.

Introduction

The field of nanotechnology is one of the most popular areas for current research and development in basically all technical disciplines. This obviously includes polymer science and technology and even this field the investigators cover a broad range of topics [1]. In Polymers, the nanoclays have been used to reinforced thermoplastics like Polypropylene to improve its properties. These improvements can include high moduli, increased strength and heat resistance, decreased gas permeability and flammability, and increased biodegradability of biodegradable polymers. However these properties are strongly influenced by how the clay is dispersed in the polymer.

Many reserchers have been studied the effects of nanocomposites, specially nanoclays, in the properties and stiffness of thermoplastics materials. János Móczó et. al [2,8] have studied that the characteristics of all heterogeneous polymer systems including composites containing either micro or nanofillers are determined by four factors: component properties, composition, structure and interfacial interactions. The most important filler characteristics are particle size, size distribution, specific surface area and particle shape, while the main matrix property is stiffness. Segregation, aggregation and the orientation of anisotropic particles determine structure. Interfacial interactions lead to formation of a stiff interphase considerably influencing properties. Interactions are changed by surface modification, which must be always system specific and selected according to its goal. Under the effect of external load inhomogeneous stress distribution develops around heterogeneities, which initiate local micromechanical deformation processes determining the macroscopic properties of the composites.
Jyi-Jiin Luo et. al [3] investigated polymer/clay nanocomposites consisting of epoxy matrix filled with silicate clay particles. They conclude that dramatic enhancements can be achieved in stiffness and thermal properties in these nanocomposites with small amounts of particle concentration. Thostenson et. al [4] described that Multi-scale hybrid composites have also been produced using nanoclay as reinforcement for the matrix material and Subramaniyan et. al [5] measured the off-axis compressive strength of S2 glass fiber (Vf=35%) reinforced vinyl ester resin with the addition of nanoclay particles. The motivation of adding nanoclay to a resin matrix is for enhancing the resin stiffness. The benefits of such improvement have been demonstrated in the compressive strength of fiber composites, which is influenced by the matrix shear modulus. Srinath et. al declared that dispersing nanosize particles in a polymer matrix induces superior mechanical properties compared to traditional macro fillers [6]. Nanolevel reinforcement also effects the tribological properties and needs to be clearly understood before using in practical applications. Nylon 6 with 5% organoclay was prepared by melt intercalation technique. A pin-on-disc type tribometer is used for evaluating the friction and wear behavior. It is found that the Nylon 6 nanocomposites have superior tribological properties than unfilled polymer. Formation of uniform tenacious transfer layer by Nylon 6 nanocomposite on the counterface contributes to the reduction in coefficient of friction and specific wear rate. Nylon Nanocomposites exhibited high wear resistance compared with the neat Nylon. Pattanayak et. al [7] said the composite with 5 wt% clay provided a 60% increase in tensile strength and 50% increase in strain at break, while the tensile modulus increased only by 15% over TPU. Yves Termonia [8] developed a numerical finite-difference model for the study of the factors controlling the properties of composites reinforced with platelets and fiber-like nano-inclusions. The approach provides a comprehensive treatment of the dependence of composite modulus and strength on the shape of the inclusions and the interrelated effects of their orientation, volume fraction, aspect ratio, modulus and interfacial properties with the matrix. At the same volume fraction, we find that platelets are generally more efficient than fibers in improving composite modulus. David W. Litchfield have studied the effect of nanoclay concentration on the molecular orientation and drawability of poly(ethylene terephthalate) PET was examined. Both Young's modulus and tenacity showed the maximum improvement at a 1% wt loading of clay, which was shown to coincide with the maximum amount of molecular orientation [9]. Anthoulis et. al declared that a special class of polymer/organoclay nanocomposites has been observed to exhibit an impressive improvement in different types of properties, physical and chemical ones [10]. He presented a model that implied to formulate response of epoxy/clay nanocomposites, experimentally tested elsewhere. The model on Mori-Tanaka theory, for the estimation of the elastic stiffness tensor for composite materials, is combined with the self-consistent model of Budiansky and Wu, valid for crystal plasticity. Then the macroscopic plastic response of the heterogeneous material is linked with the microstructural parameters, i.e., the plastic behavior of the effective particle. The model was proved to successfully describe the tensile response of the epoxy/clay nanocomposites with varying clay weight fraction.
Santos et. al said that the properties of polypropylene nanocomposites are dependent on the quaternary ammonium salt in the montmorillonite (MMT). A nanocomposite with C-15A, which

has a high cation exchange capacity (CEC), exhibits an increase in its impact properties, while one prepared with C-20A, which has a low CEC, shows an increase in the flexural modulus. The DMA results showed that while the organoclay improved the modulus of PP, the Tg was decreased slightly [11].

When polymer slide against metal counterfaces, transfer films are formed. This is also the case when sliding occurs between a polymer and another polymer. In the latter case, the transfer of material has been documented by infrared studies which show that material transfer occurs from a polymer of low cohesive energy density to one of higher cohesive energy density. The transfer filme formed on a non-polymer counterface is governed by the counterface material and roughness, and of course the sliding conditions. The growth of transfer film with the number of passes is presented and the effect of counterface roughness is examined. It is shown that when polymer are modified, such as by the addition of fillers, the transfer film effects the tribological behaviour. Some fillers affect the development of transfer film and enhance its adhesion to the couterface. Such fillers reduce the wear rate of polymer, often drastically. On the other hand, there are many fillers which have no such effect on the trasfer filme and wear in these cases is increased [12].

During the ejection phase of the injection moulding cycle the parts are mechanically forced to separate from the moulding surfaces, this aspect being more relevant with deep cores. The design of the injection systems depends on factors such as the draft angles, the surface finish, and the properties of the moulding material at the ejection temperature and the dimensioning of actuation devices. Knowledge of the friction properties of the metal and plastics surfaces is important to optimaze the ejection system. The coefficient of friction at the ejection stage depends on the superface texture of the core and the temperature at ejection [13].

Lam et. al discuss the mechanical performance of nanoclay/epoxy composites (NCs) through micro-harness and abrasive tests. It was found that the hardness and wear resistance of NCs increased with increasing nanoclay content of up to 4 wt%. The improvement of mechanical properties of the NCs by increasing nanoclay content is explained by the degree of agglomeration of nanoclay clusters inside the NCs through SEM and XRD investigations [14].

K. Kanny et al. in their study deals with the wear rates and quasi-static mechanical properties of polypropylene (PP) infused with layered organo-modified montmorillonite nanoclays. Test results show that PP infused with 2 wt% of organo-modified montmorillonite gives improved mechanical strength, higher fracture toughness, and lower wear rates. Transmission electron microscopy shows that the structure of the modified nanocomposite changes from an exfoliated structure at 1 wt.% nanoclay loading to an intercalated structures at 5 wt.% nanoclay loading. The general improvement in properties, which includes but not limited to the thermal barrier properties, may be attributed to the change in structure [15].

Franciso J. Carrión et al. said the nanocomposite (LS2 + 3% B 2010) presents a 88% reduction in friction and up to two orders of magnitude reduction in wear rate with respect to the base polymer. The new nanocomposite has been characterizated by transmission electron microscopy (TEM) and X-ray diffraction (XRD), and its thermal and dynamic mechanical properties have been determined by differencial scanning calorimetry (DSC), thermogravimetric analysis (TGA) and dynamical mechanical analysis (DMA) techniques. The nanocomposite shows a uniform disperson of the nanoclay as pointed out by two different statistical methods. The good tribological performance of the new nanocomposite is attributed to this uniform microstructure and to the increase in the nanoclay stacking distance [16].

Du-Xin Li et al. have studied about reinforced polyamide 6-polyurethane (PA6-PU) block copolymers with different short glass fiber proportions were prepared by monomer casting (MC) technology. Tensile strength of the composites increased with the addition of glass fibers, but notch impact strength decreased. The glass fiber reinforcement was found effective in reducing the coefficient of friction and the wear rate [17].

Experimental

Materials and Processing. The samples were got by Injecton molding. The materials used were a Polypropylene Homopolymer, Nanoclay for Polyolefin Nanocomposites in percentages of 2%, 6% and 10% and a Polypropylene Homopolymer with content of 10% and 30% of glass fiber reinforced. For the Physical characterization was used DSC and DMA, for the mechanical characterization through the thickness was used Triboindenter Hysitron equipped with MRNP device. For the study of friction coefficients was used mouldfriction device.

Physical characterization. Injected samples were characterized by Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA).

DSC was performed in a Perkin Elmer Pyris 1 device at a heating rate of 10ºC/min between -30°C and 200°C. Melting temperature (Tm) was determined as the peak temperature, and crystallization degree (x_c) was estimated as:

$$x_c = \frac{\Delta H_m}{\Delta H^0 (1-\phi)} 100 \quad (1)$$

Where ΔH_m is the apparent enthalpy of fusion per gram of material, ΔH^0 is enthalpy of fusion for totally crystalline material (209 J/gr for PP), and ϕ is the relative amount of reinforcement.

DMA was performed in a Perkin-Elmer dynamic mechanical analyzer (DMA-7) at a fixed frequency at 1 Hz in a three-point bending mode, while increasing the temperature from -40 to 120ºC at a heating rate of 10ºC min^{-1}. Tg was obtained from tan δ peak and heat distortion temperature (HDT), defined as the temperature at which a 0.25 mm deflection occurs under 0.46 MPa, was measured by thermal mechanical analysis using the method developed by Scobbo [18]. This method translates the standardized load and deformation into modulus assuming approximately linear stress–strain behavior for small loads and deformations typically specified in the standards. For the displacement of 0.25 mm and load of 0.46 MPa, this translates into log(modulus in Pa units) = 8.9.

Mechanical characterization through the thickness. Mechanical properties were assessed by means of micro-indentation tests. Injection molded samples were cut, included in an epoxi resin block and polished using grid paper up to 4000.

Micro-indentations were performed using a Triboindenter Hysitron equipped with MRNP device. Indentations were made using a diamond Berkovich tip under load controlled conditions. A trapezoidal loading function was used to diminish creep effects on the unloading response. Two set of experiments were carried out. The first one was conducted to determine local properties through the injection molded sample thickness in PP and nano-composite samples. A maximum load of 20mN was applied at a rate of 2mN/s, then the load was held during 20s and finally the load was removed at 2mN/s. Indentations were performed at 5 different locations on the sample (see dashed lines in Fig 1). In each location a pattern of 25 indentations was applied. The second set was performed to obtain average properties of the skin and core regions of micro and hybrid-composites. A maximum load of 1N was applied at a rate of 100mN/s, then the load was held during 20s and finally the load was removed at 100mN/s. Indentations were performed at 10 different locations on the sample (following the dotted lines in Fig 1).

The obtained load-displacement curves were analyzed in terms of the Oliver-Pharr approach to extract both reduced elastic modulus and hardness values [cita]. Unloading data between 60% and 100% of maximum load were used in the fitting procedure. The tip geometry was considered ideal.

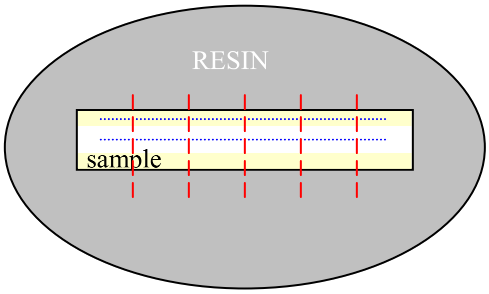


Fig 1 - Scheme of indentation distribution locations for the two set of experiments.

Tribological characterization Friction é normally understood as the resistance to relative motion offered by bodies in contact. In injection moulding the bodies in contact are steel moulding surfaces and polymer mouldings. The concept of coefficient of friction to lead some simple terms: the static friction may be larger than kinetic (dynamic) friction, friction force is proportional to normal force and friction force is independent of the contact area. The variables used at mouldfriction were 65°C as ejection temperature, contact pressure was 5 bar, replication temperature was 120°C and It was used 3 different roughness Ra 0,2; 0,6 and 0,8.

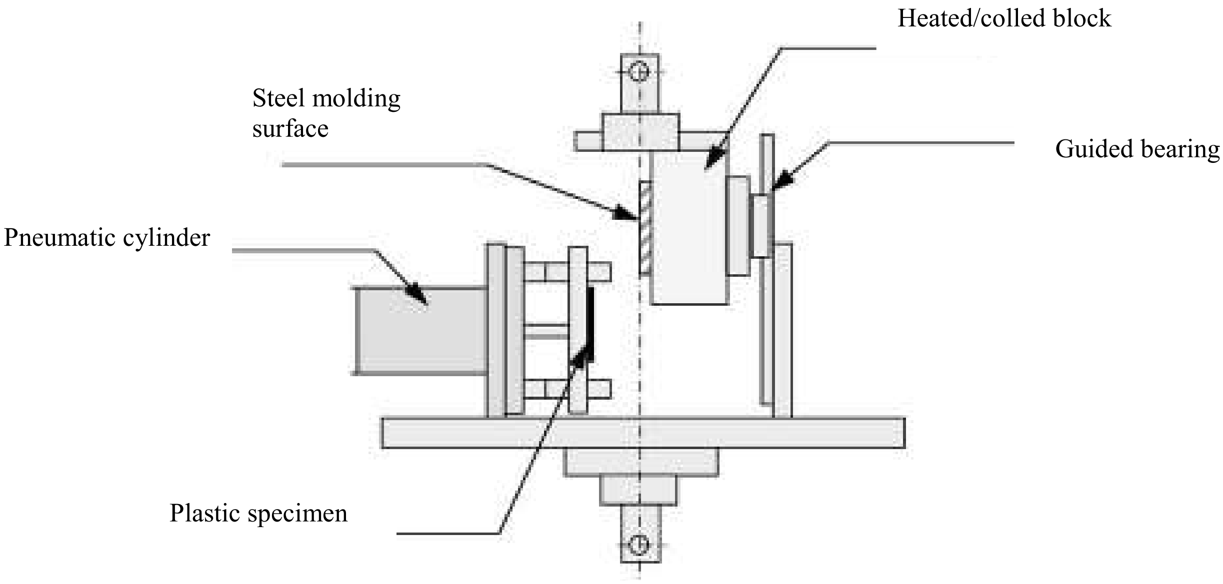
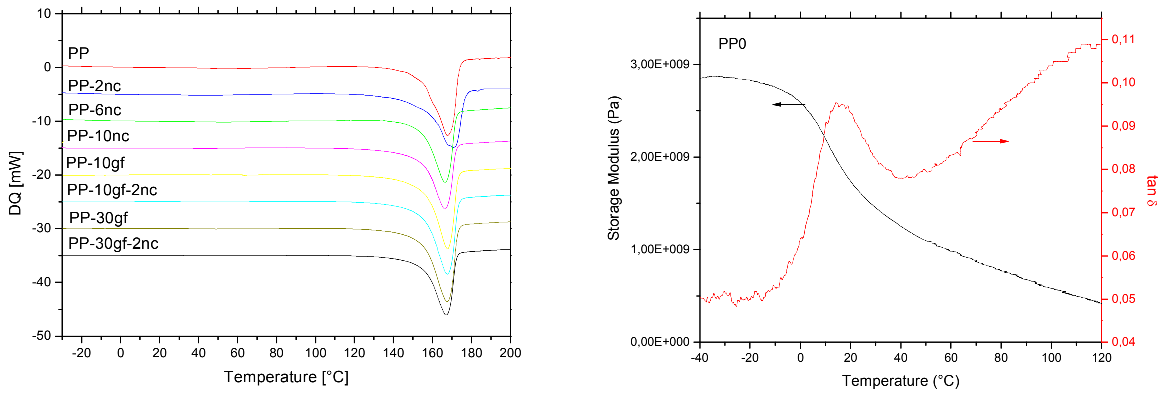


Fig. 2 - Technical drawing of the friction technical equipament

The testing routine for the determination of the coefficient of friction using the prototype equipment Moulfriction was described by Pouzada et al. (13) and includes the following steps: 1) heating of the moulding surface up to the replication temperature, 2) stabilization of the temperature, 3) application of contact pressure to get surface replication, 4) cooling down to the testing temperature and 5) friction test at selected cross-head speed. The testing equipment is composed by functional systems for control of temperature, contact pressure for replication of the surface and for testing, and movement guiding.

Results and discussion

Physical characterization. Typical DSC and DMA curves are shown in Fig. 3 and obtained properties are depicted in Table 1. It was observed that x_c diminished with the addition of nanoclay (nc). With the incorporation of glass fiber (gf), this diminishing disappeared irrespective of the presence or absence of nanoclay. On the other hand, Tg and HDT increased with the addition of nanoclay, reaching a maximum for 6%. The incorporation of glass fibre noticeable increased HDT, while Tg remained practically unaffected.



a) b)

Fig 3 - Typical curves. a) DSC, b) DMA (only one material is shown in this plot in order to make it clear).

Table 1. Physical properties of studied materials.

Material	Tm [°C][(1)]	x_c [(1)]	Tg [°C] [(2)]	HDT [°C] [(2)]
PP	167.7	42.5	16.1	77.8
PP-2nc	170.7	41.1	17.5	79.3
PP-6nc	166.5	39.5	20.7	84.1
PP-10nc	165.6	34.4	15.5	63.4
PP-10gf	167.7	41.8	15.8	121.9
PP-30gf	167.6	40.0	16.5	123.5
PP-10gf-2nc	167.7	41.7	21.4	120.1
PP-30gf-2nc	167.2	44.1	19.7	129

[(1)] Determined by DSC
[(2)] Determined by DMA

Mechanical characterization through the thickness. Fig. 4a shows typical load-depth data obtained in through the thickness experiments for samples with nanoclay. Curves can be divided into two main groups: one belonging to indentations performed on the epoxy resin and the other to indentations made on the sample. The maximum penetration depth was about 1.5µm for the former, while it varied from 2.5µm to 3.5µm depending on the composition of the analyzed sample and also on the relative location of the indentation through the sample thickness. Little scatter was observed in this set of experiments.

Regarding samples with glass fiber, experiments performed at 20mN resulted widely scatter due to the presence of glass fibers and their comparable dimensions with indentation imprints. In order to reduce scatter the maximum indentation load was increased up to 1N (Fig 4b). However, some discontinuities were still observed in the loading curves but not during unloading. This was probably originated when the tip became directly in contact with a glass fiber even tough the size of the indentation imprint is larger than the fiber dimensions.

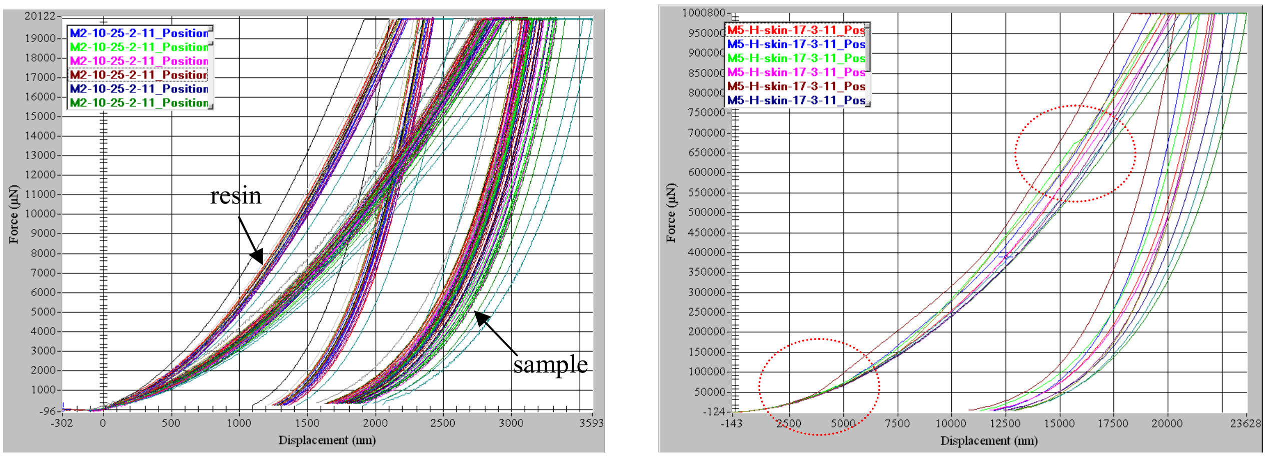


Figure 4. Load-depth curves in through the thickness experiments. a) PP-10nc b) PP-10gf

Fig. 5 shows typical results in the form of reduced elastic modulus and hardness raw values plotted as a function of the relative thickness position through the sample. Relative thickness position values between 0 and 1 correspond to the analyzed sample, and the remaining to the epoxy resin. The dimensions of the skin-core regions were evaluated from these patterns, and values are reported in Table 2. It should be pointed out that the skin layer thickness resulted independent on the clay concentration. Regarding PP-GF composites, the optical inspection indicated that at the skins the fibers become aligned to the mold surface by the high shear stresses close to it while at the core the fibers become perpendicular to the mold surface. This result is in agreement with previous results by Martinez Gamba et al. [19]. The same observation was made in the hybrid-composite samples.

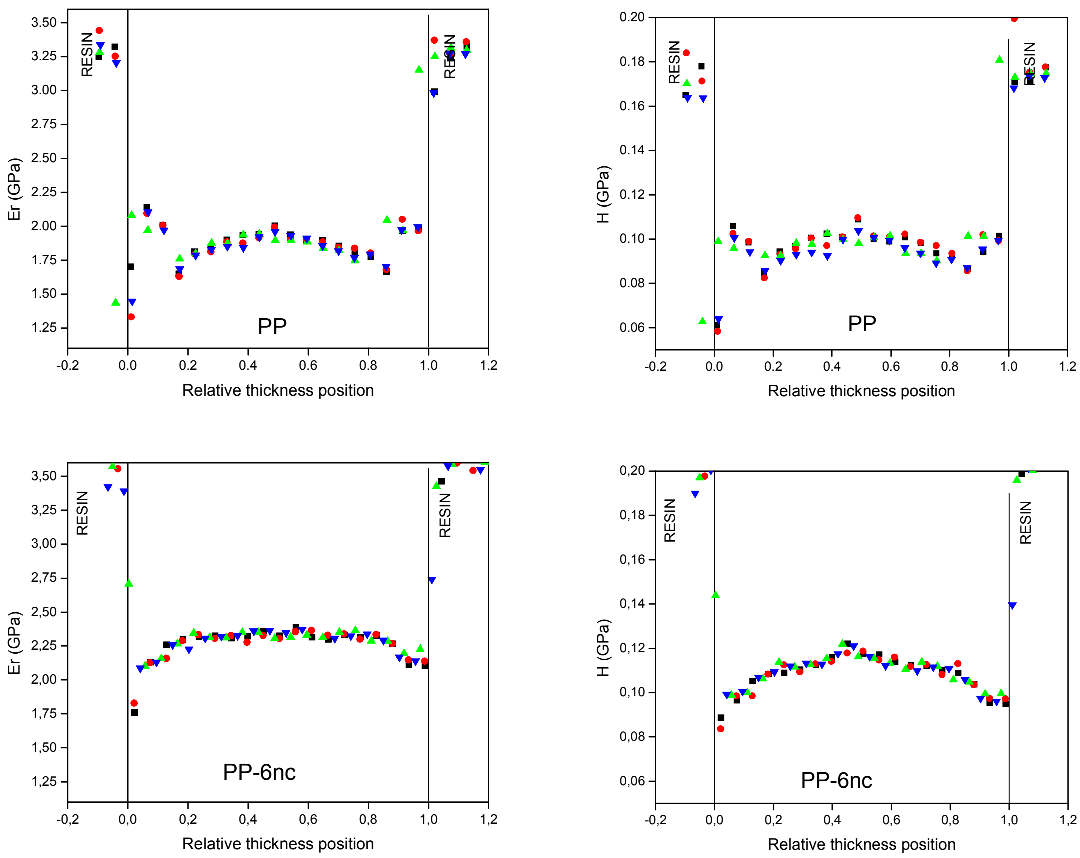


Figure 5. Typical raw reduced elastic modulus (left side) and hardness (right side) values plotted as a function of the relative thickness position through the sample

Table 2. Skin-core dimensions in PP-nc composites according to the mechanical evaluation.

Material	Skin thickness (mm)	Core thickness (mm)
PP-2nc	0.261	1.343
PP-6nc	0.216	1.428
PP-10nc	0.259	1.344

The average values of Er and H for the skin and core regions are shown in Fig. 6. It was observed that the properties of the skin and core regions of the injection molded PP sample are similar. Nano-composites become stiffer and harder than PP due to the reinforcement effect of the clay. However, the change in properties appears to be independent on the clay concentration, at least in the studied useful range. It was found that the incorporation of 2%wt. clay is enough to promote changes in mechanical properties and further incorporation is unnecessary. Also, the incorporation of clay promotes a big differentiation in the properties of the skin and core regions (note that in contrast to the PP samples, properties of the skin and core regions greatly differ for the nano-composites). The enhancement in properties is larger in the core region than in the skin zone. It should be remembered that hardness is directly related to the yield stress of the material by a constraint factor, so an increase in hardness is related to an increase in yield stress.

Regarding PP-gf composites, it was found that PP-gf micro-composites are stiffer and harder than PP samples. Elastic modulus and hardness values increase while increasing the glass fiber content. However, taking into account that the reduced elastic modulus of the glass fiber is about 70GPa, the GF-PP micro-composites does not exhibit properties improvement according to the direct rule of mixtures.A large differentiation on properties between the skin and core regions develops, being the core stiffer and harder than the skin especially at the higher glass fiber concentration. It appears that there is not a synergetic increase in elastic modulus and hardness in the hybrid-composites neither in the skin nor in the core regions. The increment seems to be additive.

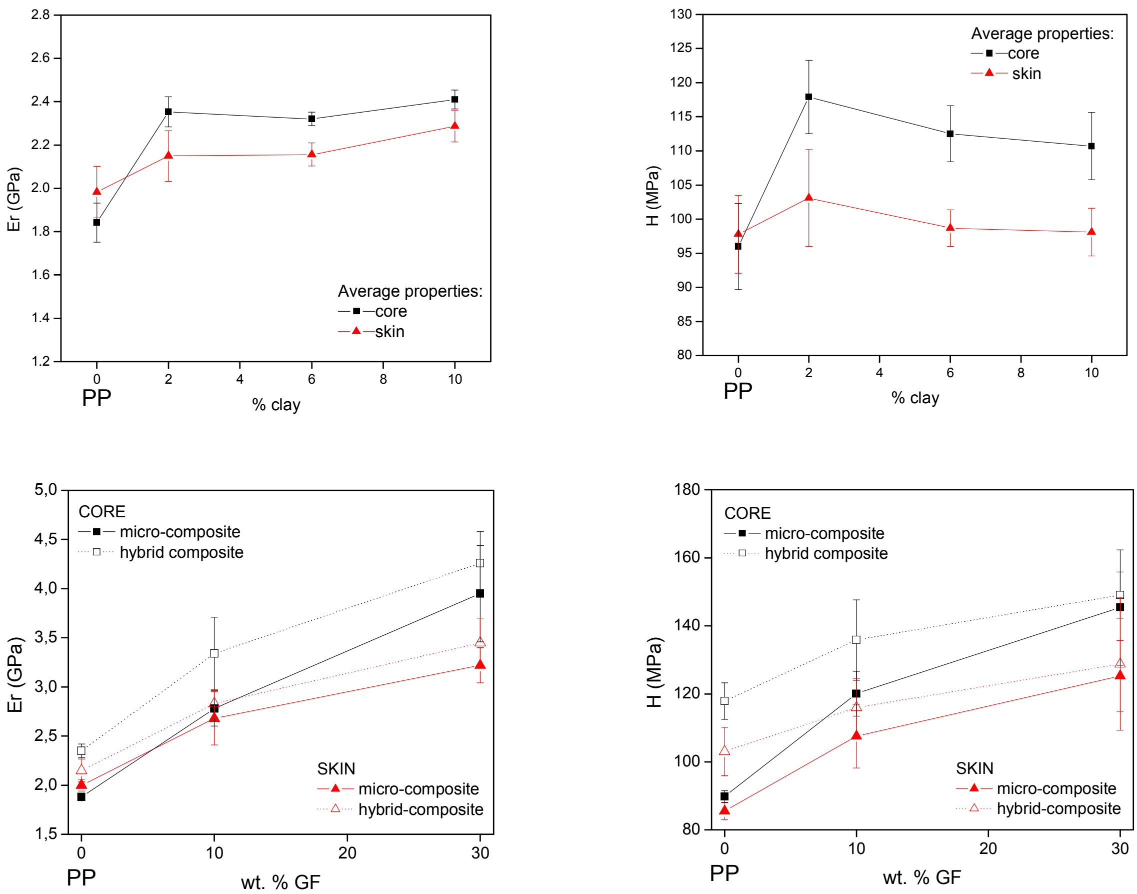


Figure 6. Average reduced elastic modulus (left side) and hardness (right side) values for the skin and core regions.

Tribological Characterization

The aim of this experiment was to determine the friction coefficients between steel and polymer in the ejection temperature for several materials. The results can be seen below, in Fig. 7.

We can observe in this picture that PP 30% glass fiber and PP 30% glass fiber with 2% nanoclays present the highest values for the friction coefficient to any roughness next to pure PP, so when the roughness is bigger, the friction coefficient also increase. The results also show that with increase the percentage of nanoclays, generally, decrease the friction coefficient. We can also note that to 10% glass fiber with and without 2% nanoclays, present practically the same valor of friction coefficient. It seems that the nanoclays act as a lubrificant decrease the friction.

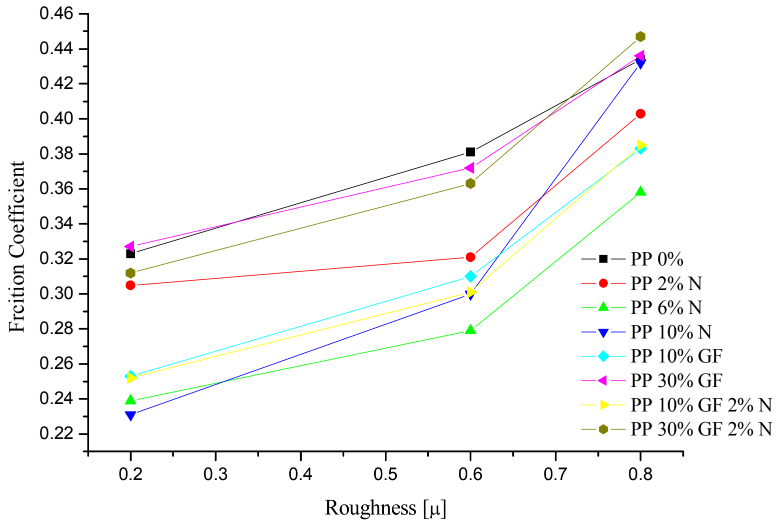


Fig. 7 – Friction coefficients for several materials in relation to Roughness

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Conclusions

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