

# Effect of processing conditions on morphology and mechanical properties of compatibilized polypropylene nanocomposites

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## Abstract

This work focuses on the influence of processing conditions on the nanocomposites structure, i.e. intercalated or exfoliated, and on the enhancement of mechanical properties of polypropylene (PP) nanocomposites. These nanocomposites were prepared using the melt intercalation technique in a co-rotating intermeshing twin screw extruder. In order to optimise processing conditions, both screw speed and barrel temperature profile were changed. The role of the compatibilizer (maleic anhydride grafted polypropylene) was also studied. The results obtained show that the barrel temperature is a very important parameter: using lower processing temperature, the apparent melt viscosity and, consequently, the shear stress are higher and, therefore, the exfoliation of the clay is promoted. Even using optimised processing conditions, exfoliation of clay can be achieved only when an high compatibility between polymer and clay exists: the PP nanocomposites containing maleic anhydride show an exfoliated structure and a sensible enhancement of mechanical properties while PP nanocomposites without compatibilizer show a structure mainly intercalated and a lower improvement of mechanical properties.

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## 1. Introduction

Manufacturers have long since filled polymers with particles in order to improve the stiffness and toughness of materials, to enhance their barrier properties and their resistance to fire and ignition. Addition of particulate fillers sometimes imparts drawbacks to the resulting composites such as brittleness or opacity. Nanocomposites are a new class of composites, that are particle-filled composites for which at least one dimension of the dispersed particles is in the nanometer range. The most interesting aspect of the use of nanofillers is the very low amount of filler that has to be added to the polymer in order to be effective. In this way, the undesired effects due to the introduction of the traditional amounts of inorganic additives, which are very high, can be avoided. Polymer layered silicate nanocomposites (PLSN) were reported in the patent literature as early as 1950 [1]. However, it was not until Toyota researchers [2,3] began a

detailed examination of polymer layered silicate composites that nanocomposites become more widely studied in academic, government and industrial laboratories. Since the early Toyota works, which are based on the formation of nanocomposites in situ during polymerisation of caprolactam, many works have been published on polymer nanocomposites. These works show that several strategies have been considered to prepared PLSN, i.e. intercalation of polymer or pre-polymer from solution, in situ intercalative polymerization and melt intercalation. Among them, the most versatile and environmentally benign technique is the melt intercalation owing to the absence of organic solvents, because it is compatible with current industrial processes, such as extrusion and injection moulding. It can be used for polymers, which were previously not suitable for in situ polymerisation or solution intercalation.

Many works on PLSN focus on the importance of chemical surface modification of the clay employed (usually montmorillonite) in order to increase the compatibility between clay and host polymer. The role and importance of processing conditions are the subject of very few papers. Until recently, the literature contains no summary conclusions about the optimum processing conditions needed in

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order to obtain polymeric nanocomposites. Regarding polypropylene, several works on the preparation of nanocomposites via melt blending may be found in literature (reported in Ref. [4]), but these studies have not addressed the issue of how the resulting structure is affected by the design of the mixing device and processing conditions. Most studies were conducted for direct melt compounding process under intuitive processing conditions. Some works on the influence of the processing conditions on the properties of nanocomposites can be found in literature: Dennis et al. [5] studied polyamide 6 and showed that the potential properties improvement usually depends on a combination of the proper chemical treatment of the clays and optimized processing. Incarnato et al. [6] studied the influence of the extrusion rates on the properties of polyamide 6. About polypropylene, any exhaustive study cannot be found: Tidjani et al. [7] focused on the influence of the presence of oxygen during the preparation of polypropylene-*graft*-maleic anhydride nanocomposites while Wang et al. [8] analysed the effect of the shear stress on the dispersion of clay in polypropylene matrix processed via dynamic packing injection moulding (DPIM).

Today, polypropylene (PP) is one of the most widely used polyolefin polymers; it has no polar groups in the chain and then its direct intercalation or exfoliation in the silicate galleries is very difficult. Efforts were made to improve the mixing of clay in PP by using functional oligomers as compatibilizer. Usuki et al. [9] first reported a novel approach to prepare PP nanocomposites using a functional oligomer (PP-OH) with polar telechelic OH groups as compatibilizer. Several studies [10–12] reported the use of maleic anhydride grafted PP as compatibilizer. In both case the interaction between filler and polymer is enhanced by a strong hydrogen bonding between OH or COOH groups and the oxygen groups of silicate [13].

In this paper we report the effect of several processing conditions on the properties of OMLS-PP (organically modified layered silicate polypropylene) nanocomposites. The nanocomposites were prepared through melt intercalation in a co-rotating twin screw extruder, using several processing conditions: barrel temperature profile as well as screw speed were changed. Both pure polypropylene and polypropylene-*graft*-maleic anhydride (PP-*g*-MA) were filled with several amounts of an organically modified layered silicate. The morphology as well as mechanical properties of the materials prepared were characterised by use of transmission and scanning electron microscope (TEM and SEM, respectively), X-Ray diffraction (XRD) and

mechanical tests. Therefore, the aim of this work is the study of the influence of compatibilizer and processing conditions on the extent and degree of dispersion of the modified nanofillers in PP matrix.

## 2. Experimental part

### 2.1. Raw materials

Pure polypropylene (PPH 7062) and polypropylene-*graft*-maleic anhydride (Fusabond MD551D) were supplied by Total Petrochemicals and DuPont de Nemours Int., respectively. The melt flow index of such materials are 12 g/10 min (230 °C/2.16 kg) and 22.5 g/10 min (190 °C/2.16 kg), respectively. The polypropylene-*graft* maleic anhydride contains 1 wt% of maleic anhydride (MA). An organo-modified clay (Dellite 72T, powder), that is a ditallow-dimethyl-ammonium ion modified natural montmorillonite (MMT), with a mean particle size of 8 µm was supplied by Laviosa Chimica Mineraria (Livorno, Italy). Thermogravimetric analysis of OMLS, carried out in oxidizing atmosphere (from 30 to 900 °C, 15 °C/min), showed weight loss of about 35 wt% between 200 and 600 °C, due to water and to the organic fraction introduced as compatibilizer.

### 2.2. Preparation of the nanocomposites

PP nanocomposites were prepared using melt blending technology in an intermeshing co-rotating twin screw extruder ( $D=42$  mm,  $L/D=40$ ), set up with medium shear configuration modular screw. This kind of extruder gives higher degree of back mixing with respect the counter-rotating intermeshing or non-intermeshing extruders. The use of low or high shear intensity configuration screw have not been studied as Dennis et al. [5] already reported that excessive low or high shear intensity may cause poor delamination and dispersion. The filler used was previously pre-dry-blended in a turbo-mixer. Nanocomposites based on pure PP and PP containing 6 wt% of PP-*g*-MA were prepared. During extrusion, two different barrel temperature profiles (Fig. 1), screw speeds (250 and 350 rpm) as well as filler contents (3.5 and 5 wt%) were used. In the following we refer to the different processing conditions as high/low temperature profile or screw speed. The samples will be called as HL for the samples obtained at higher temperature profile and lower screw speed, as HH for the samples

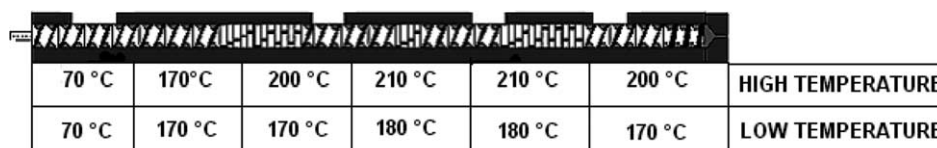


Fig. 1. Barrel temperature profiles.

obtained at higher temperature profile and higher screw speed, etc. In sample names, the number after the letters refers to the weight % filler content: for example, LH-3.5 refers to a sample processed at lower temperature profile, higher screw speed, filled with 3.5 wt% of organically modified MMT. Full details are reported in Table 1.

### 2.3. Characterisation

The specimens for mechanical characterisation were compression moulded. Tensile modulus, yield stress and strain, stress and elongation at break were measured using a dynamometer (Galdabini, mod. Sun 2500); the tests were carried out according to ISO 527. The flexural modulus was determined using the same dynamometer in a 3-point loading test, according to ISO 128. Notched-Izod impact tests were carried out at 23 °C with a pendulum-type impact tester (Ceast, Resil 25) according to ASTM D256. The mechanical properties reported in the following were the average of at least five measurements.

The dispersion of the clays on a microscopic scale was examined using a Philips XL30 scanning electron microscope (SEM) and an operating voltage of 20 kV. Samples were taken from cryofractured specimens obtained via compression moulding, dried and gold-coated. The degree of intercalation and delamination of the clay were monitored by transmission electron microscopy (TEM, Philips mod. EM 208) and X-ray diffraction (XRD, Philips mod. X'PERT PRO). Samples for TEM analyses were cut from ultra-thin specimens using a Leica Ultracut UCT

microtom. XRD analyses were carried out in reflectance mode with a  $\lambda=0.1541837$  nm.

## 3. Results and discussion

### 3.1. Mechanical properties

The effect of the processing conditions, clay content as well as compatibilizer on the tensile modulus can be analysed using the results showed in Fig. 2, where the proportional increases of tensile modulus with respect to neat PP are reported. All nanocomposites prepared showed a significant improvement of tensile modulus with respect to unfilled PP; the enhancements are strictly related to the processing conditions, the filler content and the presence of compatibilizer. Considering the same processing conditions, the elastic modulus is higher in presence of compatibilizer for both filler contents (3.5 and 5 wt%) owing to the greater interaction between filler and polymer. This implies that the stress is much more efficiently transferred from the polymer matrix to the inorganic filler, resulting in a higher increase in tensile modulus. Similar results were obtained for 5 wt% filled PP and 3.5 wt% filled PP-g-MA for the same processing conditions. The results for 5 wt% filled PP-g-MA were extremely better: the proportional increase of tensile modulus is about 130%.

Considering the results for the same polymeric matrix processed at different conditions two parameters shall be analysed: the effect of shear rate and the extent of diffusive processes. When in fact the clay are melt blended into a polymer, the clay platelets are slide apart from each other by the shear stress in the extruder; otherwise the platelets separation can be increased also by the diffusion of polymer chains into the clay galleries. The highest increase of tensile modulus was obtained using higher screw speed, i.e. higher shear rate: the sample named HH and LH were always better than HL and LL, respectively. Analysing different barrel temperature profile the data showed that the better results

Table 1  
Processing conditions and filler content of the nanocomposites prepared

Samples	Temperature profile	Screw speed (rpm)	Filler (wt%)	T at die end (°C)
PP-HH	Higher	350	0	201
PP-HL	Higher	250	0	204
PP-LH	Lower	350	0	172
PP-LL	Lower	250	0	170
PP-HH-3.5	Higher	350	3.5	202
PP-HL-3.5	Higher	250	3.5	203
PP-LH-3.5	Lower	350	3.5	173
PP-LL-3.5	Lower	250	3.5	170
PP-HH-5	Higher	350	5	206
PP-HL-5	Higher	250	5	204
PP-LH-5	Lower	350	5	172
PP-LL-5	Lower	250	5	170
PP-g-MA-HH	Higher	350	0	209
PP-g-MA-HL	Higher	250	0	209
PP-g-MA-LH	Lower	350	0	171
PP-g-MA-LL	Lower	250	0	175
PP-g-MA-HH-3.5	Higher	350	3.5	208
PP-g-MA-HL-3.5	Higher	250	3.5	208
PP-g-MA-LH-3.5	Lower	350	3.5	177
PP-g-MA-LL-3.5	Lower	250	3.5	180
PP-g-MA-HH-5	Higher	350	5	207
PP-g-MA-HL-5	Higher	250	5	206
PP-g-MA-LH-5	Lower	350	5	175
PP-g-MA-LL-5	Lower	250	5	175

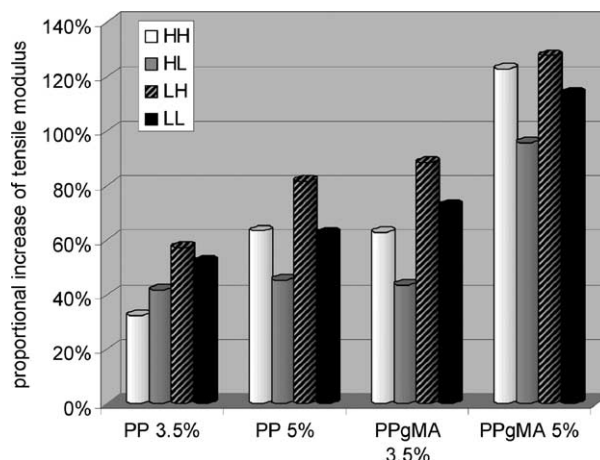


Fig. 2. Proportional increase of tensile modulus.

were obtained at lower barrel temperature profile: the samples named LH are always better than HH samples and the samples LL are always better than HL. Therefore, the lower the barrel temperature profile and the higher the screw speed, the higher will be the enhancements of tensile modulus. Otherwise, for the material analysed the barrel temperature profile cannot be further decreased because the polymer exits from the die end (Table 1) at a temperature very close to its melting point (163 °C). The effect of filler content, compatibilizer as well as processing conditions on the tensile yield stress and strain were also analysed. No significant influence of those parameters was revealed on yield stress: it was about 31 MPa and the differences between filled and unfilled materials were lower than 3%. Some decreases of yield strain were found out: while the elongation at yield was about 10.5% for unfilled PP, it decreased to about 9.5% for PP nanocomposites and about 8.5% for PP-g-MA nanocomposites. The reduction of yield elongation may be due to the greater interaction between filler and polymer matrix, which probably leads to a lower polymeric chain mobility making the material more rigid. The greater interaction should be responsible also for the lower elongation at break that was showed for all the specimens tested: in the better case, it dropped from 550% for a neat PP down to 290% for a 3.5 wt% filled PP, 80% for a 5 wt% filled PP, 50% for a 3.5 wt% filled PP-g-MA and 40% for a 5 wt% filled PP-g-MA.

The flexural modulus is reported in Fig. 3. The flexural modulus of 5 wt% filled PP, 3.5 and 5 wt% filled PP-g-MA for the same processing conditions (except the LH conditions) are very similar. The effect of processing conditions on flexural modulus is similar to that on tensile one: the proportional increase of both tensile and flexural modulus for the same material may increase significantly, depending on the processing conditions used. Anyway, better results were obtained using the lower barrel temperature profile and higher screw speed.

The proportional increase (with respect to pure PP) of IZOD impact strength for all the nanocomposites prepared

are reported in Fig. 4. It can be seen that no specimen showed IZOD value lower than that of unfilled polymer; the increases are higher at higher filler contents; in particular for 5 wt% PP-g-MA nanocomposites, processed at lower temperature and higher screw speed (LH), the increase is about 50% with respect to pure PP. The enhancement of IZOD is due to the fact that the exfoliated or intercalated clay layers in nanocomposite play a role in hindering the crack path caused by impact. During impact, the stress in the sample may be dispersed by the intercalated or exfoliated layers, which have higher strength and modulus than the matrix, thus making the IZOD impact strength higher. It was reported that this effect is much more important when a high interaction between filler and polymer is obtained [14,15]. In fact, when maleic anhydride is used, i.e. a greater interaction between nanoclays and polymers is achieved, the IZOD values, for the same filler content, are higher for the PP compatibilized matrix. Besides the effect of compatibility, another competitive aspect shall be considered: the degree of crystallinity. Friedrich [16] and Ouederni et al. [17] found, in fact, that an increase in crystallinity or spherulite size could decrease the toughness. DSC analyses of the nanocomposites prepared (which will be reported in a future work) showed that the crystallinity is fairly similar for all filled samples and then any significant variations of IZOD values can arise from this parameter.

These different observations showed that PP-g-MA nanocomposites combine high stiffness and good ductility at least up to a clay loading of 5 wt%; moreover the mechanical characterisation showed that greater enhancements can be obtained processing the material at the lower barrel temperature profile and higher screw speed. Considering that, for the same barrel temperature profile, the increase of screw speed leads to the increase of shear stress exerted on the polymer and to a simultaneous decrease of the residence time, the results obtained showed that the first parameter (i.e. the shear stress) is much more influent on the extent of intercalation and delamination than the second one (i.e. the residence time). As it was showed [5] that the

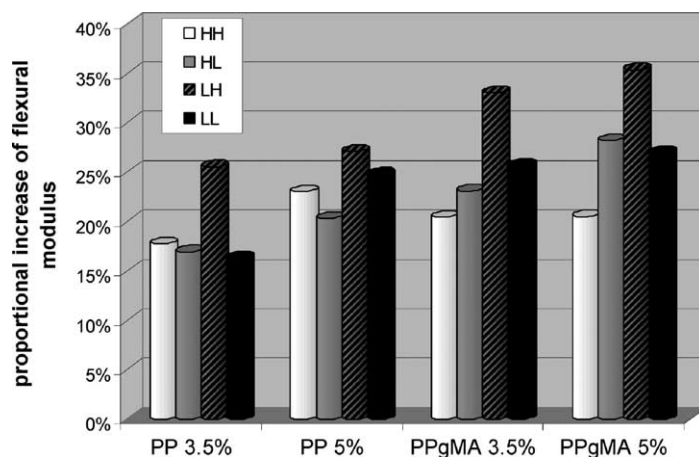


Fig. 3. Proportional increase of flexural modulus.

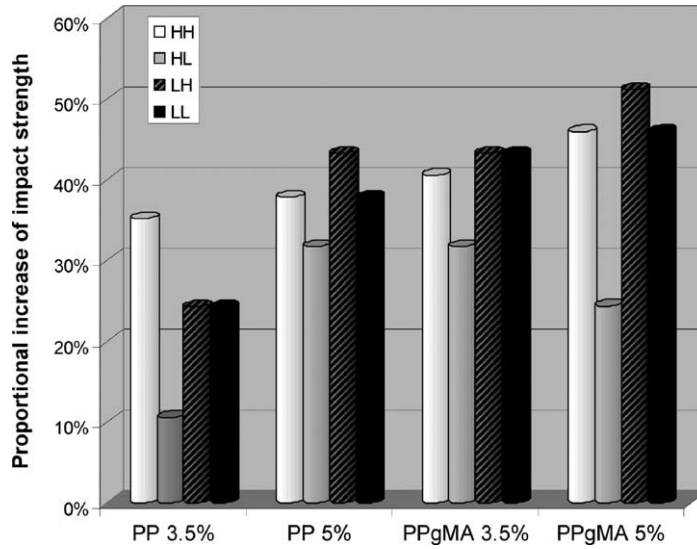


Fig. 4. Proportional increase of impact strength.

residence time is a controlling factor when diffusion processes of the polymer in clay galleries shall take place for the intercalation or delamination to occur, we can state that for the system analysed the controlling factor is the

intensity of the shear stress transmitted to the polymer instead of the diffusion processes. This observation is in agreement also with the fact that the better results are obtained at lower barrel temperature profile. In this case, in

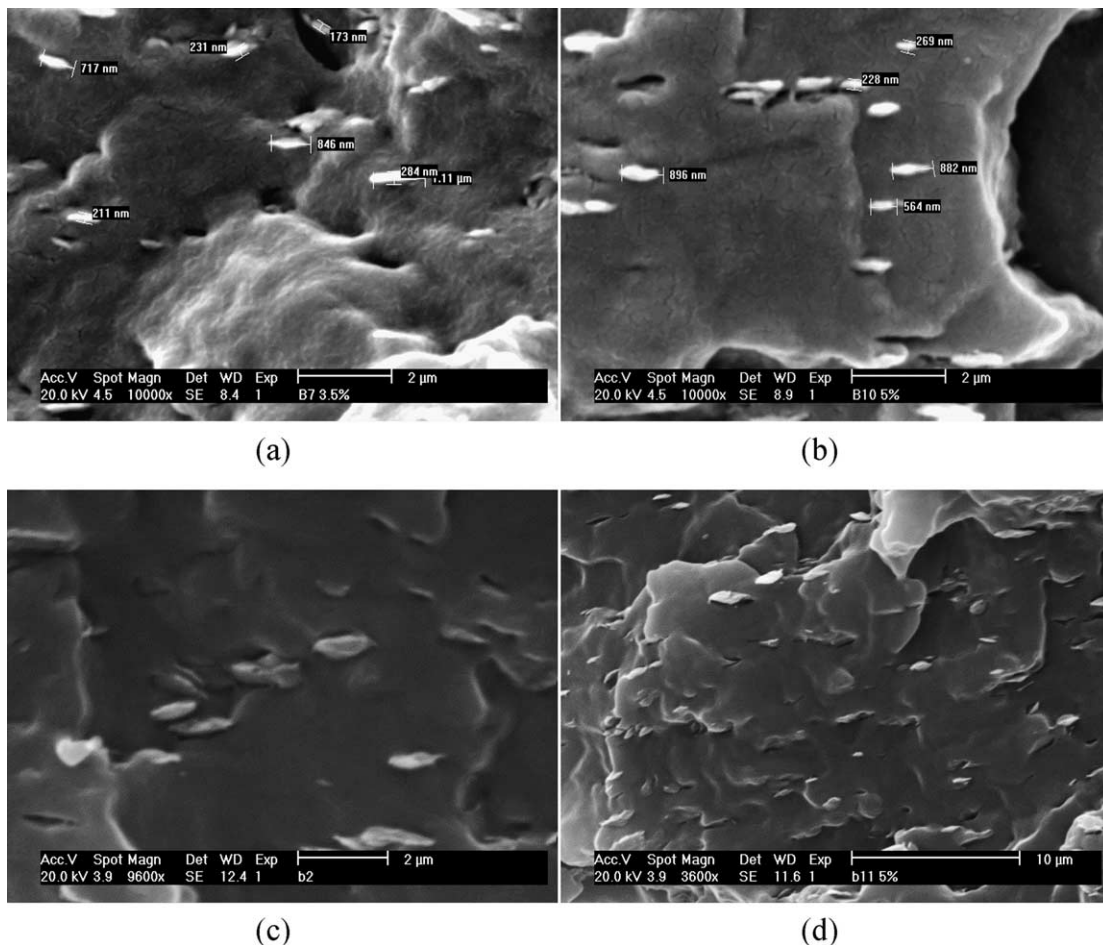


Fig. 5. SEM micrograph of PP-LH-3.5 (a), PP-LH-5 (b), PP-HL-3.5 (c) and PP-HL-5 (d) samples.



fact, the melt viscosity is higher and thus, for the same shear rate, the shear stress exerted on polymer is higher than that transmitted at higher barrel profile temperature. Otherwise, as the diffusion processes are not the controlling factor, the reduction of processing temperature does not lead to any worsening effect on the final structure and properties of the material. The diffusion processes are not extremely important for the PP analysed in this work probably because of the high melt flow index of the polymer, i.e. for its high fluidity.

### 3.2. Morphological characterisation

The effect of processing conditions on the dispersion of the filler in neat PP and PP containing PP-g-MA was studied by use of SEM. Fig. 5(a)–(c) and (b)–(d) show the micrographs of 3.5 and 5 wt% filled nanocomposites, respectively, for different processing conditions. The dispersion of the clay is not uniform and the smallest lateral dimension of the clay tactoids measured about 200 nm; similar results were obtained for the other PP based nanocomposites. In deep contrast, for PP-g-MA based nanocomposites (Fig. 6), the clay is uniformly dispersed in

the polymer matrix; the average lateral dimension of the clay is about 100 nm. Similar results were obtained also for the other PP-g-MA based nanocomposites, which were processed in different conditions. Elemental analysis (EDAX) of random sample of particles seen in the micrographs showed that these areas are highly enriched in silicon and thus, deeming these particles as tactoids. Because SEM magnification is not able to show intercalated or exfoliated clay platelets, the morphological characterisation of nanocomposites prepared were carried out also by use of TEM. These analyses may be usefully used in order to study the extent of intercalation or exfoliation of the nanocomposites obtained. TEM micrographs at low magnification showed a uniform dispersion of the filler in the polymer matrix, whatever the filler content analysed. In order to assess the presence of tactoids, intercalated and/or exfoliated structure higher magnifications are required. The high magnification micrographs of PP-LH3.5 and PP-LH5, i.e. the nanocomposites based on neat PP, which showed the better mechanical characteristics, are reported in Fig. 7(a)–(d), respectively. Considering that the dark are the silicate platelets, it is evident that the presence of unseparated montmorillonite layers (i.e. tactoids) and some areas where

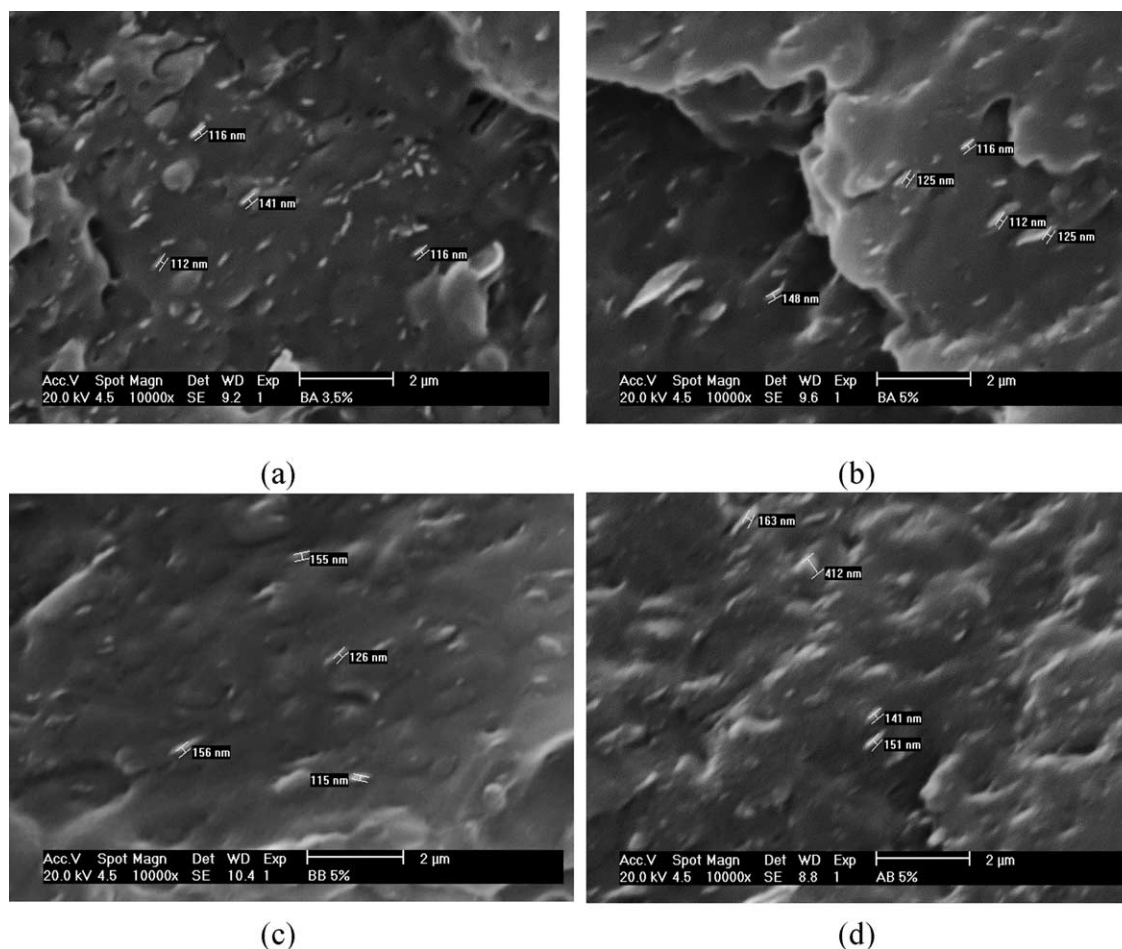


Fig. 6. SEM micrograph of PP-g-MA-LH-3.5 (a), PP-g-MA-LH-5 (b), PP-g-MA-LL-5 (c) and PP-g-MA-HL-5 (d) samples.

small amount of polymer moved into the gallery spacing between the clay platelets but caused less than 2–3 nm separation between the platelets; these areas are known as intercalated zones. TEM micrographs of PP-g-MA based nanocomposites, for both 3.5 (Fig. 8(a) and (b)) and 5 (Fig. 8(c) and (d)) wt% filled samples, showed instead, a higher degree of intercalation. Moreover, PP-g-MA nanocomposites showed also exfoliated structure: the clay layers are separated in a continuous polymer matrix and in some areas individual clay layers are recognizable.

The morphological structure of nanocomposites were finally studied by use of XRD. The XRD patterns of the samples, which were characterised by the better mechanical properties are reported in Fig. 9. The XRD curve of PP-LH-5 nanocomposite showed a slight shift of the peak towards lower angles, thereby indicating that the distance between clay platelets had become greater. XRD curves of nanocomposites containing maleic anhydride showed the presence of two diffraction peaks at low angles: one is fairly shifted at lower angles with respect to pure MMT while the second is reported at slightly larger angles. The shift of the first one is related to the increase of distance between clay

layers. Moreover, also an increase of disorder of the silicate layered structure, related to the presence of an intercalated-delaminated configuration, was revealed by the broadening and decrease in intensity of the diffraction peak. Considering the position of the second peak a possible coalescence of clay platelets can be inferred; it is possible that during processing some alchilic chains have been degraded and thus, the interlayer spacing has become lower.

Using the Braggs relation the interlayer spacing can be evaluated; the results for the nanocomposites analysed are reported in Table 2. As can be seen, the distance between clay platelets increases of about 0.5 nm for PP nanocomposites and about 1.4 nm for compatibilised nanocomposites.

#### 4. Conclusions

This work shows the importance of both compatibilizer and processing conditions on the extent of the enhancement of mechanical properties of PP nanocomposites. Considering different processing conditions, the results obtained show that the shear stress exerted on polymer is much more

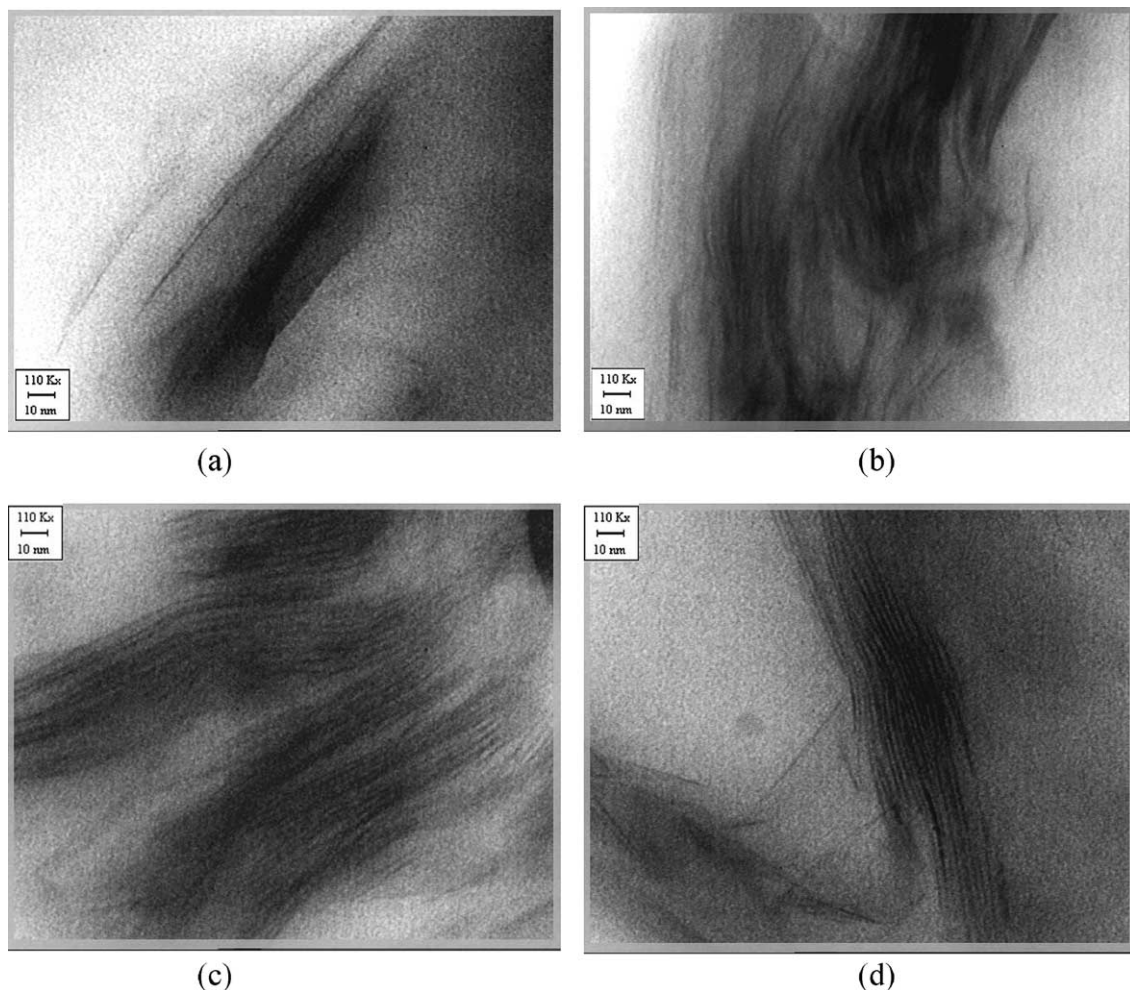


Fig. 7. TEM micrographs of PP-LH-3.5 ((a) and (b)) and PP-LH-5 ((c) and (d)) samples.

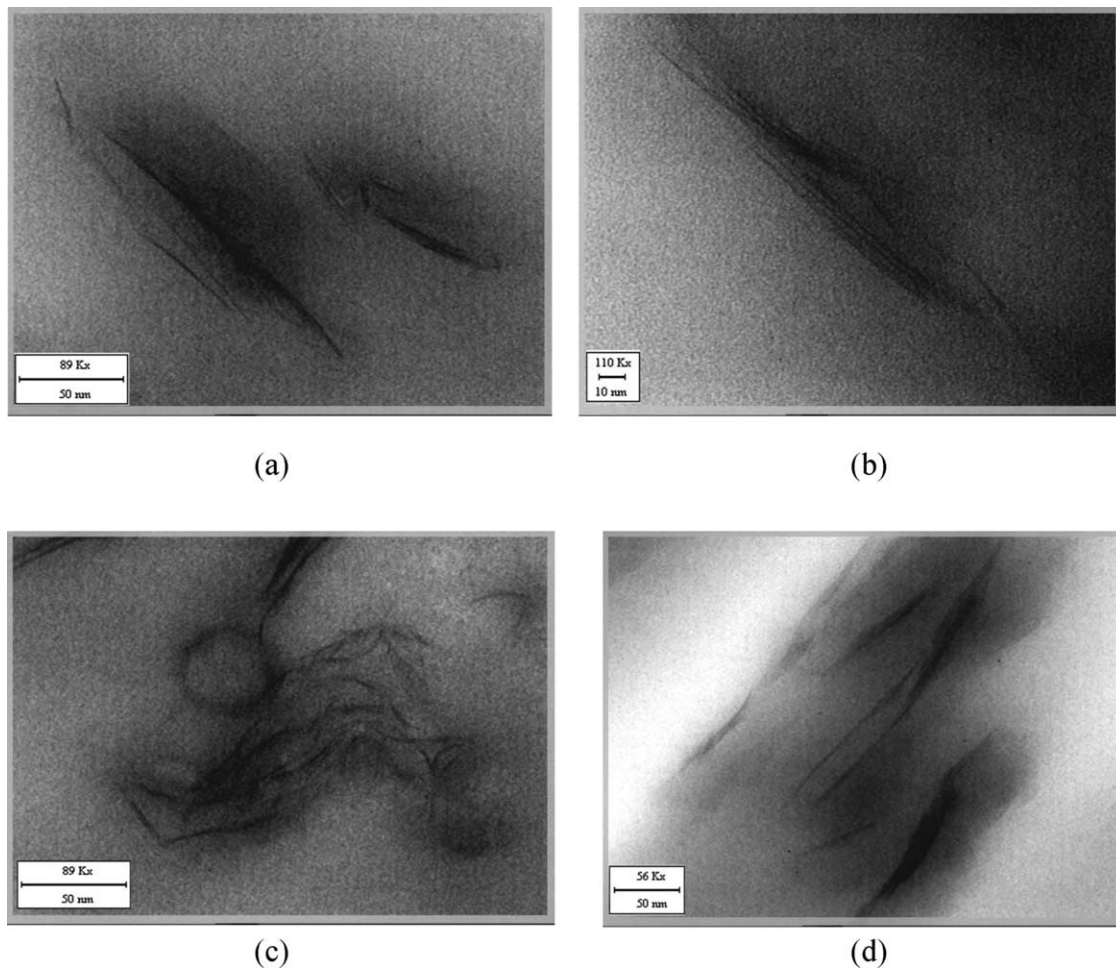


Fig. 8. TEM micrographs of PP-g-MA-LH-3.5 ((a) and (b)) and PP-g-MA-LH-5 ((c) and (d)) samples.

influence on the extent of intercalation and delamination than the residence time, probably because the diffusion process (which is related to residence time) of the polymer chains into clay galleries is not the controlling factor. The better

results were obtained using processing conditions that maximize the shear stress exerted on the polymer, i.e. at higher screw speed and lower barrel profile temperature.

As can be inferred from morphological characterisation, even using optimised processing conditions, a high degree of intercalation or exfoliation of clay can be achieved only when a high compatibility between polymer and clay exists: the PP nanocomposites containing maleic anhydride show an intercalated or exfoliated structure and a sensible enhancement of mechanical properties while PP nanocomposites without compatibilizer show the presence of intercalated zones and some tactoids and lower improvement of mechanical properties. The results also show that the impact strength values of nanocomposites are higher than those of pure PP; this is a great advantage of nanofillers

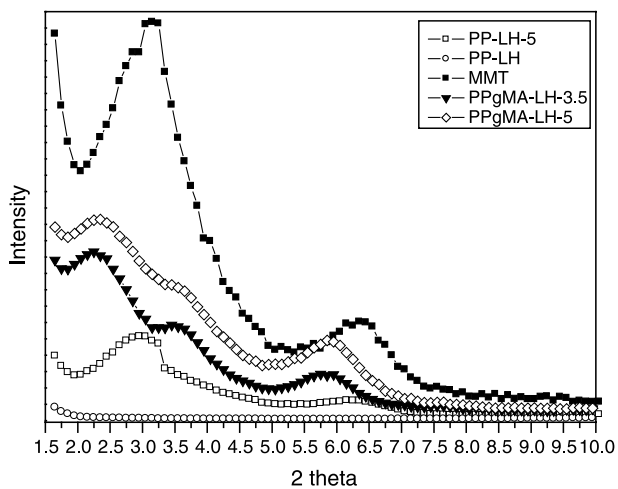


Fig. 9. XRD analyses of montmorillonite (MMT), PP-LH, PP-LH-5, PP-g-MA-LH-3.5 and PP-g-MA-LH-5 samples.

Table 2  
Interlayer spacing for some nanocomposites

Samples	Interlayer spacing (nm)
MMT	2.56
PP-LH-5	3.00
PP-g-MA-LH-3.5	3.93
PP-g-MA-LH-5	3.84



with respect to traditional micrometric fillers, which generally cause a sensible decrease of this property. Using PP-g-MA nanocomposites, processed at suitable conditions, a material that combines high stiffness and good ductility can be obtained.

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