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Low density polyethylene/silica nanocomposite foams. Relationship between chemical composition, particle dispersion, cellular structure and physical properties

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Abstract

This paper presents the production and characterization of polymeric nanocomposite foams based on low density polyethylene (LDPE) and different contents of silica nanoparticles. The properties of these foamed materials are conditioned by the properties of the polymer matrix and by the characteristics of the cellular structure. In general, when adding nanoparticles several improvements are obtained in both the solid nanocomposite and the cellular structure. However, the achievement of these potential improvements is conditioned by the level of filler dispersion and by the compatibilization degree between the particles and the polymer. This work analyzes the effects on the dispersion and compatibilization levels of adding, or not, a compatibilizer agent (linear low density polyethylene grafted with maleic anhydride, LLDPE-g-MA), with the aim of understanding the structure and properties of the foamed materials produced from these composites. A modified version of the pressure quench method was used to produce the foamed samples. This method allows obtaining net-shaped foams adequate for analyzing both their microstructure and mechanical properties. Results show that for this particular system, the incorporation of the LLDPE-g-MA compatibilizer does not promote a better dispersion but implies significant differences in terms of nucleating efficiency and reinforcing effect of the nanoparticles. While for solid nanocomposites the higher degree of bonding polymer/nanoparticle promoted by the presence of the compatibilizer translates into a positive mechanical reinforcing effect, for foamed nanocomposites, such high level of compatibilization mitigates the nucleating effect of the nanoparticles. This translates into poorer mechanical properties in the foamed samples containing the compatibilizer agent.

1. Introduction

During the last years, polymer nanocomposites foams have focused the attention of both scientific and industrial communities. The combination of foaming technologies and polymer nanocomposites can lead to a new class of multifunctional materials [1].

The multifunctional role played by nanoparticles in polymeric foams lies in an improvement of the overall properties of the foam by acting at two levels. On the one hand, nanoparticles can modify and optimize the cellular structure and on the other hand, they are able of improving the morphology and properties of the solid polymer matrix comprising the cell walls [1,2].

Nanoparticles can contribute to obtain improved cellular structures because they act as nucleating agents and they can also modify the polymer rheology inducing

strain hardening and thus, favoring gas retention during the foaming process [1–4]. Foams with reduced cell sizes and more uniform and narrower cell size distributions usually exhibit enhanced physical properties [5–7].

Considering that cell walls of foams are in the micron and sub-micron regime, reinforcing them with nanoparticles can be especially beneficial due to their nanometer dimension [1]. The presence of nanoparticles can induce some very well-known effects on the polymer matrix such as polymer morphology modification (increased crystallinity in semicrystalline polymers), improved thermal stability or enhanced mechanical response, among others [8–12].

However, the obtaining of all these potential improvements is typically conditioned to achieve a proper dispersion and compatibilization of the nanofillers [1,2]. Several authors have concluded that when nanofillers are dispersed properly an effective nucleating effect, accompanied by an improvement in physical properties, is obtained. For instance, Zhen et al. [13] demonstrated the high impact of the filler delamination level on the polymer foamability. They observed a higher cell nucleation efficiency with the exfoliated nanoclays than with the intercalated ones in both polystyrene (PS) and poly (methyl-methacrylate) (PMMA). Urbanczyk et al. [14] dealt with the foaming of styrene acrylonitrile (SAN)/clay nanocomposites using supercritical CO₂. They concluded that while for intercalated nanocomposites nucleating effect of nanofillers was negligible, for completely exfoliated nanocomposites the cell density reached values two orders of magnitude higher than that obtained for the neat polymer foam. Other interesting study was carried out by Shen et al. [15]; they produced nanocomposite foams based on PS filled with different types of nanoparticles: carbon nanofibers (CNFs), single-walled carbon nanotubes (SWCNTs) and clays. After analyzing the dispersion level of each type of filler, they calculated the nucleation efficiency of each nanomaterial. It was found that the nucleation efficiency was (in percentages) 1.97 for CNFs, 9.06×10^{-5} for SWCNTs and 7.37×10^{-4} for nanoclays. Those results were in agreement with the dispersion degree reached by each type of filler; while SWCNTs and clays were forming aggregates, CNFs were well dispersed.

The effect of adding a compatibilizer agent has also been carefully analyzed. Lee et al. [16] and Seraji and co-workers [17] performed similar studies using low density polyethylene (LDPE) as polymeric matrix and montmorillonite (MMT) as filler. They concluded that the addition of a compatibilizer led to a clay exfoliation and only in this case, the nucleation effect induced by MMT was effective.

In addition, it is possible to find in scientific literature examples correlating the effective nucleation of well dispersed nanoparticles with an improvement in the physical properties of nanocomposite foamed systems. Wang and co-workers [18] analyzed the structure and mechanical properties of thermoplastic polyurethane (TPU)/clay nanocomposite foams. They found that nanoclays acted as effective nucleating agents which led to improved mechanical properties, with respect to the unfilled material. Other example is provided by Chen et al. [19]; they measured the compressive response of PMMA filled with multi-walled carbon nanotubes

(MWCNTs). A significant increase in elastic modulus was detected with the addition of 1 wt% of MWCNTs due to the improvements obtained in the cellular structure of these foams.

As it has been demonstrated with the previous examples, it is possible to find a substantial amount of papers analyzing the role played by nanoclays, SWCNTs, MWCNTs or CNFs as nucleating and reinforcing elements in different polymeric foamed systems. Nevertheless, as far as the author knows, the number of scientific studies concerning the production and/or characterization of polymeric foams filled with silica nanoparticles is more limited.

Fumed silica is a fine, white, amorphous powder, which is odorless and tasteless. It exhibits an extremely large surface area and smooth nonporous surface, which could promote strong physical contact between the filler and the polymer matrix [10,20]. In addition, fumed silica tends to form aggregates and particle-particle interactions due to the presence of silanol groups (Si-OH) on their surface and because of their very high surface energy (caused by their large surface area) [10].

Due to this strong tendency of silica particles to form aggregates, obtaining a good dispersion with the existing compounding techniques is not a simple task. Particularly, this is especially tedious for non-polar polymers such as polyethylene (PE). Two are the most commonly approaches used to overcome this problem. The first one consists on modifying the surface of silica nanoparticles (typically with silane coupling agents) and the second one consists on using functionalized polymers (polymers grafted with maleic anhydride) as compatibilizers between the filler and the polymeric matrix [1,2,10,20].

Silica/polymer foamed systems described in literature use one of these approaches to ensure a correct dispersion of the nanofiller. Zhai and co-workers [21] added surface modified silica particles to polycarbonate (PC). They obtained a good dispersion of the filler which led to an effective reduction of cell size and to an increase of two orders of magnitude of cell density. Yeh et al. [22] analyzed the nucleation efficiency of raw and vinyl modified silica particles, concluding that only the modified ones could serve as active heterogeneous nucleating agents in PMMA. Gorem et al. [23] mixed PMMA with fluorinated and bare silica nanoparticles of different sizes. They concluded that fluorination of the silica surface reduced the critical free energy of nucleation resulting in a reduction in the cell size. Zhai et al. [3] used a polypropylene-grafted maleic anhydride (PP-g-MA) compatibilizer to improve the adhesion between non-modified silica particles and linear polypropylene (PP). They observed multisilica aggregates well dispersed due to the addition of the coupling agent. Moreover, they found that the addition of a small amount of nanosilica dramatically improved the foaming behavior.

All these papers are focused on analyzing the influence of silica particles at a microstructural level. However, there is little evidence of how the presence of these particles affects the physical properties of the foamed nanocomposites. As far as the author knows, for silica/polymer foamed nanocomposites, the multifunctional role of the nanoparticles and the effect of these nanoparticles on

the foam properties have not been analyzed in detail. In addition, the number of papers in which foamed nanocomposites are produced by using silica particles and non-polar semicrystalline polymers is very scarce [3,24,25]. This is another aspect in which this paper presents novel results.

Bearing all these ideas in mind, the main goal of this study is to produce solid and foamed LDPE/silica nanocomposites, containing different silica contents, to analyze the relationships between chemical composition, compatibilization level, filler dispersion, cellular structure and physical properties. For this purpose, both asurface-modified silica and a compatibilizer based on linear low density polyethylene-grafted with maleic anhydride (LLDPE-g-MA) have been used to attempt to improve the interaction between the particles and the polymer and to promote the silica dispersion level. Samples have been foamed using a slightly modified version of the pressure quench method. The characterization of these samples will provide useful information about how the chemical composition of the different nanocomposites affects them at microscopic and macroscopic levels.

2. Experimental

2.1. Materials

The polymer matrix employed was LDPE supplied by Sabic, (LDPE 2404) with melt flow index (MFI) of 3.95 g/10 min (measured at 190°C and 2.16 kg), density of 0.92 g/cm³ and melting temperature, measured by DSC, of 113.4°C. Nanosilica particles (Aerosil R-974) were kindly provided by Evonik and they presented a primary particle size of 12 nm and a specific surface area of 200 m²/g. In addition, the surface of these particles was modified with dimethyldichlorosilane. Fusabond MB-226DE from DuPont was used as compatibilizer. It is LLDPE-g-MA with MFI of 1.5 g/10 min, (measured at 190 °C and 2.16 kg), melting point of 115 °C, density of 0.93 g/cm³ and content of maleic anyhidride of 0.9% by weight. A small amount of stearic acid (Stearic Acid 301 from Renichem S.L.) was used as processing aid. In order to avoid polymer degradation, antioxidant (Irganox 1010 from Ciba) was also included. Carbon dioxide with a high purity (99.95%) was used as physical blowing agent.

2.2. Compounding of solid LDPE/silica nanocomposites

Before foaming step, solid nanocomposites have been melt-compounded in a batch mixer (Rheodrive 5000 from Haake Fisions). Compounding was carried out at a constant temperature of 130°C. A screw speed of 50 rpm was applied for 6 min.

In a first stage, two masterbatches have been produced. The first one includes a silica content of 27 wt% and 4 wt% of the compatibilizer agent. The second one is produced with the same amount of silica particles but without compatibilizer. These masterbatches were then diluted by melt blending with the LDPE, in order to obtain several compounds with different silica contents: 1, 3, 6 and 9 wt%. Solid nanocomposites containing the compatibilizer agent will be called hereafter as S-NC1, S-NC3, S-NC6 and S-NC9. Those without the compatibilizer will be referred as S-NS1, S-NS3, S-NS6 and S-NS9. The sample corresponding to solid neat polymer (without silica particles and without coupling agent) has been used as reference. This

sample will be called S-LDPE. The chemical composition of each sample is detailed in Table 1.

2.3. Foaming of LDPE/silica nanocomposites

Pellets of the two types of solid nanocomposites were compression molded in a two hot-plates press at 150°C and 4 MPa to obtain discs with 20 mm in diameter and 3 mm in thickness. These discs were used for the foaming experiments and for the characterization of solid materials.

Foaming step was conducted in a high pressure vessel using a modified version of the pressure quench method. In this modified process the solid precursors were foamed inside a cylindrical mold. The objective of preparing the foams in a mold is to produce foams with similar densities and controlled geometries [26]. A nominal expansion ratio (that is, density of the solid nanocomposite divided by the density of the foamed material) of 1.6 was fixed for all the foamed samples. Moreover, as the foamed samples present a well-defined geometry their mechanical behavior can be easily characterized.

Table 1. Chemical composition of LDPE/silica solid nanocomposites (by weight).

	SLDPE	S-NC1	S-NC3	S-NC6	S-NC9	S-NS1	S-NS3	S-NS6	S-NS9
LDPE	99.75	98.62	96.36	92.96	89.6	98.75	96.75	93.75	90.75
Silica	0	1	3	6	9	1	3	6	9
LLDPE-g-MA	0	0.13	0.39	0.79	1.15	0	0	0	0
Stearic Acid	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Antioxidant	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1

Table 2. Experimental values of density of solid and foamed nanocomposites and expansion ratio of foamed samples.

Sample	ρ solid (kg/m ³)	Sample	ρ foam (kg/m ³)	Expansion Ratio
S-LDPE	917.2 ± 3.2	F-LDPE	586.7 ± 31.2	1.56 ± 0.08
S-NC1	924.8 ± 4.5	F-NC1	624.7 ± 32.7	1.48 ± 0.07
S-NC3	937.2 ± 0.2	F-NC3	582.9 ± 31.7	1.61 ± 0.08
S-NC6	945.5 ± 2.5	F-NC6	561.6 ± 7.2	1.68 ± 0.02
S-NC9	971.5 ± 15.5	F-NC9	563.6 ± 19.1	1.72 ± 0.05
S-NS1	923.4 ± 0.5	F-NS1	649.5 ± 51.0	1.54 ± 0.11
S-NS3	944.1 ± 1.7	F-NS3	650.5 ± 41.4	1.54 ± 0.09
S-NS6	952.5 ± 1.6	F-NS6	671.9 ± 26.5	1.48 ± 0.05
S-NS9	969.9 ± 1.7	F-NS9	631.1 ± 43.4	1.58 ± 0.11

After being placed in the mold, precursors are saturated with CO₂ at 18 MPa for 40 min at a constant temperature of 135°C. Then, samples are cooled down until foaming temperature (115°C) and foamed by a rapid pressure drop. Foamed samples designation is the same as that employed with solid nanocomposites but with a capital F instead a capital S, that is, F-NC1, F-NC3, F-NC6 and F-NC9 for foamed nanocomposites containing compatibilizer and F-NS1, F-NS3, F-NS6 and F-NS9 for foams without it. Foamed neat polymer will be called hereafter as F-LDPE. Density values of solid and foamed nanocomposites as well as experimental values of expansion ratio are summarized in Table 2. As it can be observed, the experimental values of the expansion ratio are close to the nominal one (1.6), although some differences can be appreciated between the different materials. These differences could be a consequence of the difficulties found when producing foams with the same relative density from materials with a very different nature.

2.4. Characterization of solid and foamed LDPE/silica nanocomposites

Density of solid and foamed materials was determined by the Archimedes water immersion method using a high precision balance (Mettler AT 261), following the standard UNE-EN 1183/1.

In order to analyze nanosilica dispersion in solid materials, their morphology was studied using a high resolution scanning electron microscope (ESEM Quanta 200FEG). Solid nanocomposites were freeze-fractured using liquid nitrogen.

Cellular structure of foamed materials with and without compatibilizer was also analyzed by scanning electron microscopy (SEM) using, in this case, a Jeol JSM-820 scanning electron microscope. Samples were also freeze-fractured and the fractured surface was coated with a thin layer of gold. Cell size and cell density were determined using an image processing tool based on the software Fiji/Image J. More information about the procedure followed to obtain these parameters from the SEM micrographs can be found in the work of Pinto et al. [27].

Mechanical properties in compression of both solid and foamed composites were measured at room temperature and at a strain rate of 1 mm/min, following the standard ISO 604-2002. For this purpose, a universal testing machine Instron model 5500R6025, was employed. Elastic modulus (E) and collapse stress (σ_c) were obtained from the stress-strain curves.

A more detailed description of the experimental methods used to characterize the foams can be found elsewhere [28–32].

3. Results

3.1. Influence of chemical composition at microscopic level

3.1.1. Particles dispersion

As it was pointed out in the introduction, the dispersion degree of the filler in the polymeric matrix has a significant influence on the improvements accomplished by

the use of nanoparticles.

In this study, the dispersion level has been quantified through the analysis of different SEM micrographs. Fig. 1 shows several high resolution micrographs of solid LDPE/silica nanocomposites containing different amounts of silica particles. The micrographs in the first row correspond to samples with compatibilizer and the ones in the second row to samples without it.

Nanosilica particles can be appreciated in the micrographs as the bright white spots. It can be inferred from the figure that regardless of chemical composition, silica particles are not individually dispersed. They are forming well-scattered aggregates with a size between 100 nm and 200 nm. These results are in agreement with those obtained in similar studies that were performed using LDPE as polymer matrix and silica particles with similar diameters [32,33]. In addition, as it could be expected, the number of particle aggregates increases with the silica content.

However, the simple observation of these micrographs does not lead to any conclusion regarding the effect of the presence or not of the LLDE-g-MA based compatibilizer. Hence, it is necessary to perform a quantitative analysis. This analysis should be useful to determine the dispersion degree of nanoparticles and also to explain how the dispersion degree affects both microstructure and mechanical properties of solid and foamed LDPE/silica nanocomposites.

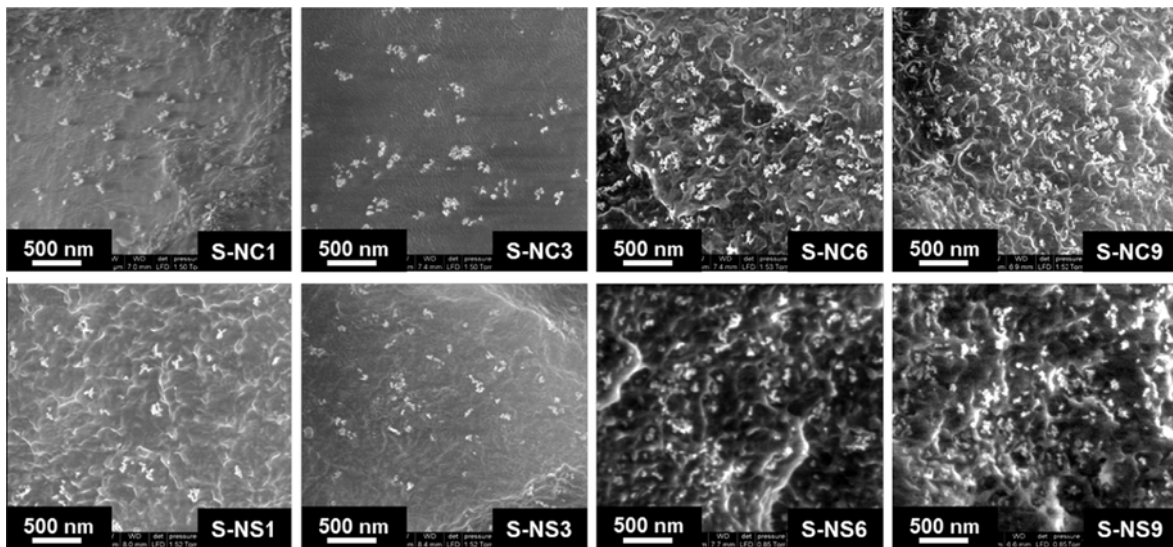


Fig. 1. High resolution micrographs corresponding to solid nanocomposites with compatibilizer (superior row) and without compatibilizer (inferior row).

The high resolution micrographs depicted in Fig. 1 have been used to quantify the real number of particles (that is, particle aggregates) per unit surface. Then, the obtained value was raised to $3/2$ to calculate the real number of particles per unit volume. Those values are summarized in Table 3. Results indicate that the quantitative analysis is in agreement with the qualitative one. The real number of particles per unit volume increases with the silica content, regardless of the

presence of the compatibilizer.

Moreover, the real number of particles per unit volume has been compared with the theoretical number of particles per unit volume. This theoretical value was calculated assuming that the silica particles were individually dispersed, that is, assuming that the silica particles did not form aggregates. Presuming a complete dispersion of the filler, the number of particles per unit volume was calculated according to the equation: $\text{particles/cm}^3 = \frac{w_p q_c}{q_p V_p}$, where w_p is the weight fraction of the particle in the composite, q_p and q_c are the densities of the particles and the polymer composite respectively, and V_p is the volume of an individual particle [21]. The values obtained from this calculation are also summarized in Table 3. As it can be observed, the values of the theoretical number of particles per unit volume are much higher than the values of the real number of particles per unit volume, regardless of the chemical composition of the samples. This fact indicates, once again, that the particles are not individually dispersed and instead they are forming aggregates.

In this point and to quantify the differences between the real and the theoretical values, the Agglomeration Ratio is defined as the ratio between these two values, that is, the theoretical number of particles per unit volume divided by the real number of particles (aggregates) present in the sample. This parameter measures the average number of individual particles comprising each aggregate. Results for all these calculations are summarized in Table 3.

The trends followed by S-NC and S-NS samples are different regarding to the increase in the particles content. While in the samples containing the compatibilizer (S-NC samples) the Agglomeration Ratio increases as silica content does, in the samples without the compatibilizer (S-NS samples) the Agglomeration Ratio does not change significantly with the silica concentration. In other words, when compatibilizer is added to the LDPE/silica nanocomposites larger aggregates are accomplished as increasing the silica content. On the other hand, when no compatibilizer is added to the polymer matrix, and only the surface modification of the silica is acting, aggregates with similar sizes are achieved independently on the particles content.

While in the samples without compatibilizer similar dispersion levels are achieved independently on the clay content, in the samples with compatibilizer the best dispersion degrees are achieved with the lowest contents of particles.

Although the relationship between the Agglomeration Ratio and the silica content depend on the chemical formulation, that is, on the fact of adding or not a compatibilizer, the overall values of the Agglomeration Ratio are very similar in the two types of composites (with and without compatibilizer). No significant differences for the Agglomeration Ratio and hence, for the particles dispersion level are found between the two different systems. Results indicate that the presence of the compatibilizer does not lead to higher dispersion degrees. It seems that the compatibilizer agent does not contribute to increase the effect of the surface modification of the silica nanoparticles.

Table 3. Analysis of dispersion degree of silica particles in the LDPE matrix: real number of particles per unit volume, theoretical number of particles per unit volume (assuming that they are individually dispersed) and Agglomeration Ratio for S-NC and S-NS samples.

Sample	Real Number of Particles/cm ³	Theoretical Number of Particles/cm ³	Agglomeration Ratio (Particles/Aggregate)
S-NC1	1.58×10^{13}	4.65×10^{15}	295
S-NC3	3.52×10^{13}	1.41×10^{16}	400
S-NC6	6.87×10^{13}	2.87×10^{16}	418
S-NC9	9.74×10^{13}	4.39×10^{16}	451
S-NS1	1.38×10^{13}	4.65×10^{15}	336
S-NS3	4.05×10^{13}	1.41×10^{16}	348
S-NS6	6.79×10^{13}	2.87×10^{16}	423
S-NS9	1.19×10^{14}	4.39×10^{16}	368

3.1.2. Cellular structure of foamed nanocomposites. Nucleating effect

One of the most important reasons to add fillers, or nano-fillers, to polymeric foams is the achievement of improved cellular structures due to their nucleating effect. The results corresponding to the observation and analysis of the cellular structure of the foamed samples are presented in Figs. 2 and 3. Fig. 2 corresponds to SEM micrographs of foamed LDPE and LDPE/ silica nanocomposites.

Both pure LDPE and LDPE nanocomposite foams exhibit isotropic closed cellular structures. Fig. 2 also shows how the addition of small amounts of silica leads to a significant reduction in cell size; moreover, this effect is more pronounced for samples without compatibilizer. From these SEM micrographs the average cell size and the cell density have been determined and the obtained results are shown in Fig. 3a (average cell size) and Fig. 3b (cell density). Results depicted in Fig. 3a indicate that just with the addition of 1 wt% of silica a reduction in cell size, with respect to the pure LDPE, of 30% is reached (from around 65 μ m to around 45 μ m). For silica contents higher than 1 wt% samples with and without compatibilizer behave in a very different way. For F-NC samples (with compatibilizer), the cell size increases as the silica content increases, reaching values even higher than that of the pure LDPE. For F-NS samples (without compatibilizer), the average cell size does not show any significant variation for samples with silica contents of 3 and 6 wt%; however, it increases slightly for F-NS9. Moreover, for F-NS samples the values of cell size are always smaller than

that of the neat polymer.

The results for cell density (Fig. 3b) are in agreement with the effects observed for the average cell size. The presence of compatibilizer leads to higher cell sizes and hence, smaller cell densities than that achieved for samples containing only surface-modified silica nanoparticles. In some cases, cell densities are even smaller than that achieved for the control sample (pure LDPE).

At this point it is necessary to analyze and quantify the efficiency as nucleating agents of silica particles in the presence or not of the compatibilizer agent. The effects of nanoparticles on the mechanisms of degeneration of the cellular structure, as coalescence phenomena, are not considered due to the high density of the cellular materials under consideration.

It is known that the ability of particles to act as nucleation sites is determined by their dispersion level along the polymer matrix and by the degree of bonding between the particles and the polymer [1,2,34]. On the one hand, the higher the

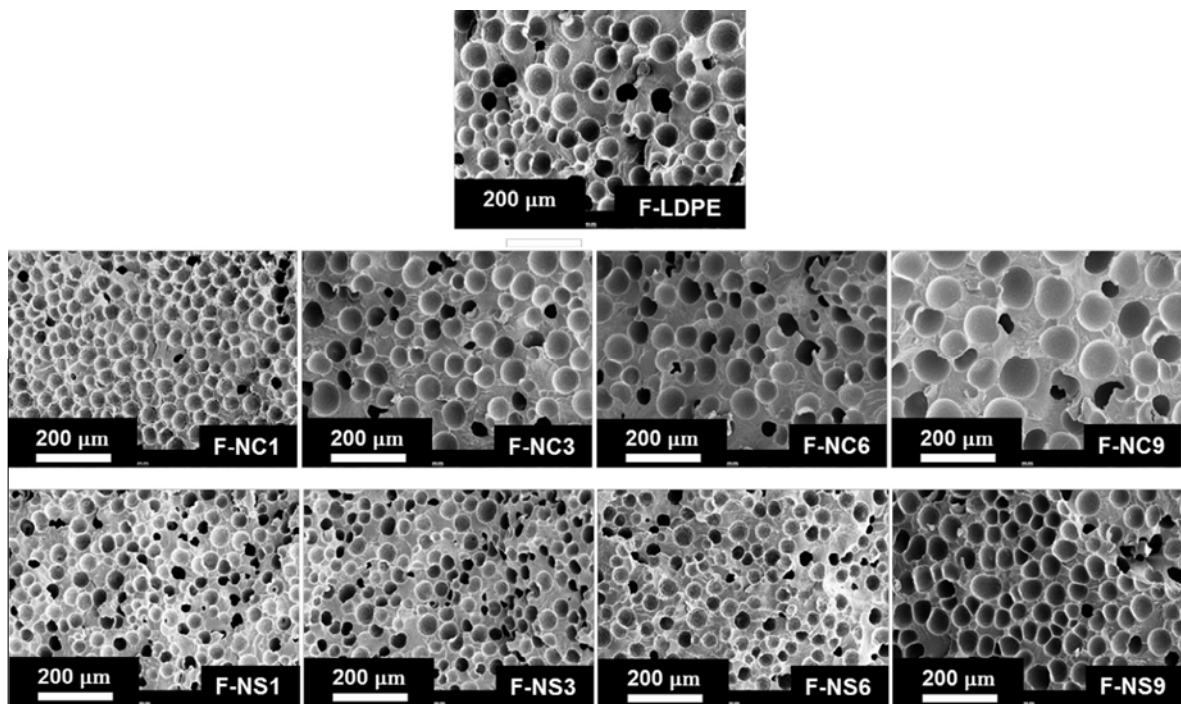


Fig. 2. SEM micrographs showing the cellular structure of foamed samples.

dispersion level the greater the nucleation effect. On the other hand, if there is a high degree of bonding between the nanoparticles and the polymeric matrix, a large amount of energy is required to force the interface apart. However, if a poor compatibilization exists, the interface between the matrix and the filler will have a lower surface tension and this will enhance cell nucleation [34].

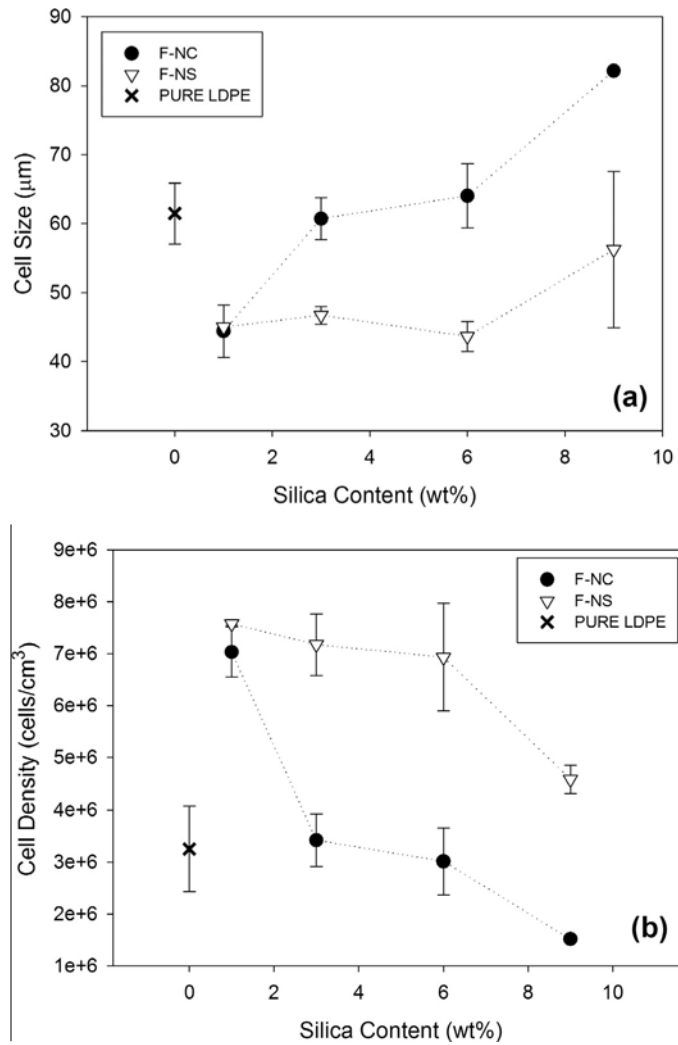


Fig. 3. Cellular structure parameters of LDPE and LDPE/silica nanocomposites. Average cell size (a) and average cell density (b).

The effect of the dispersion degree in the ability of silica particles to act as nucleating agents has been quantified by means of the Nucleation Efficiency. This parameter is defined as the ratio between the measured cell density and the potential nucleation density of the filler (number of particles per unit volume). Using the values presented in Table 3 corresponding to real and theoretical values of number of particles per unit volume, it is possible to calculate both a real and a theoretical value of nucleation efficiency for samples with and without coupling agent. Results are plotted in Fig. 4a (samples with compatibilizer) and Fig. 4b (samples without compatibilizer) together with the Agglomeration Ratio values calculated in the previous section (see Table 3). As it can be inferred from both figures, regardless of the presence of the compatibilizer, the Nucleation Efficiency considering the real number of particles per unit volume is significantly higher than that obtained from the theoretical number of particles per unit volume. In

addition, even considering the real value, Nucleation Efficiency in both systems reaches quite low values.

In samples containing compatibilizer (Fig. 4a) it can be observed that Nucleation Efficiency decreases as the Agglomeration Ratio increases. This means that the nucleating effectiveness of the particles decreases as the dispersion level decreases. All these findings are in concordance with results presented in previous studies [21,35,36]. In these works it was reported that for high silica contents, high aggregates and low dispersion levels were found, which resulted in a low nucleating effect of nanofillers.

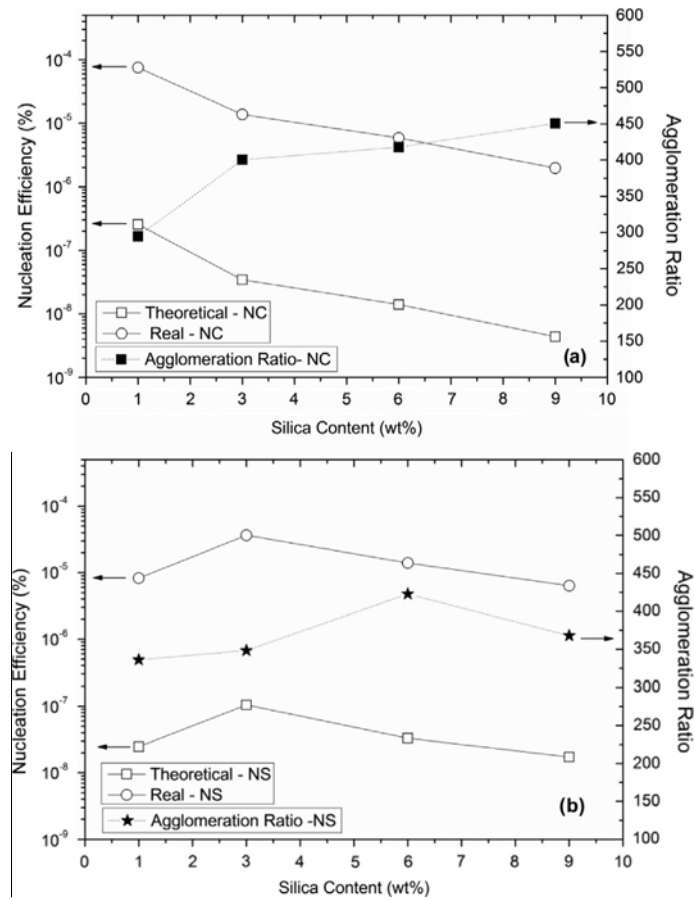


Fig. 4. Analysis of Nucleation Efficiency of silica nanoparticles in LDPE matrix for samples with (a) and without (b) coupling agent.

For samples without compatibilizer (Fig. 4b), no significant variations in Nucleation Efficiency with the changes in silica concentration were found. This is in agreement with the results obtained for Agglomeration Ratio. As dispersion levels remain approximately constant with the silica concentration, Nucleation Efficiency also does.

As it was previously mentioned, the degree of bonding between the polymer and the nanofiller also determines the effectiveness of the nanoparticles as nucleating agents. The dispersion level achieved for both types of samples is very similar (although the trends with particle concentration are not). Therefore, the big differences achieved in the overall values of cell size and cell density presented by

the materials with and without compatibilizer should be a consequence of the different degrees of compatibilization between the LDPE and the silica nanoparticles.

This effect has been analyzed by using a new parameter, the Nucleation Ratio (NR). It is defined as indicated in the following equation:

$$NR = N / N_0,$$

where N is the cell density of the sample containing the nanoparticles and N_0 is the cell density of the non-loaded control sample, neat LDPE in this case [33]. Results are plotted in Fig. 5, as a function of silica content.

The first fact that can be inferred from Fig. 5 is that regardless of the presence of the compatibilizer, the optimum silica content is 1 wt% in the two systems. The use of higher amounts of silica does not lead to major improvements in terms of microstructure.

On the other hand, the values of NR reached by the samples without compatibilizer are much higher than those reached by the samples containing it. In addition, in the system with compatibilizer it is possible to see that for some silica concentrations (6 and 9 wt%) the values of NR are lower than one. This fact indicates that the cell density of these composites is lower than that of the pure polymer (LDPE).

In general, compatibilizer agents improve the adhesion between the matrix and the filler. In this particular system, the LLDPE-g-MA based compatibilizer is enhancing the adhesion between the LDPE and the silica particles. Due to the high degree of bonding between these two phases, the energy required to force the interface apart in order to favor the nucleation process is also very high. As a consequence, a poor nucleation effectiveness of the nanofiller is reached for the samples containing the compatibilizer.

Nevertheless, in the system without the compatibilizer the adhesion between the polymer and the nanoparticles is lower, which results in a higher effectiveness of the silica as nucleating agent.

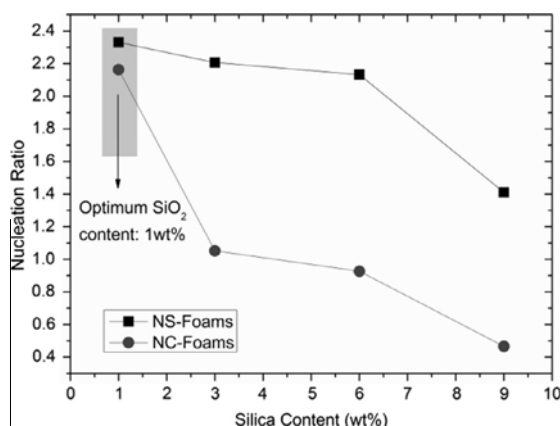


Fig. 5. Values of Nucleation Ratio for foams with and without compatibilizer.

3.2. Influence of chemical composition at macroscopic level

3.2.1. Mechanical properties of solid composites

Compression tests were performed for all types of solid LDPE/silica nanocomposites. Elastic modulus and collapse stress (Fig. 6) were calculated from the stress-strain curves [37]. In general, elastic modulus of nanocomposites is higher than that of pristine LDPE, independently of the presence of the compatibilizer. On the other hand, as silica concentration increases, different behaviors are observed for samples with and without compatibilizer. In the samples with compatibilizer (S-NC samples), the elastic modulus increases with the silica concentration up to a silica content of 6 wt%. Then, for higher silica contents, a decrease in the elastic modulus is observed. In the samples without compatibilizer (S-NS samples) the elastic modulus does not follow any clear trend with the increment in silica concentration. However, if the experimental errors are taken into account, it could be said that no important variations are found in the elastic modulus by varying the particles content, neither in the samples with compatibilizer nor in the samples without it. With regard to collapse stress, results indicate that nanocomposites reach values substantially higher than the neat LDPE. The presence of the compatibilizer can be also detected in the nanocomposites; samples with compatibilizer exhibit slightly higher values of the collapse stress than samples without it. Finally, in the same way as the elastic modulus did, the collapse stress does not vary with the particles content.

To easily compare the differences between solid nanocomposites and neat LDPE, the increment in percentage of both elastic modulus (DE) and collapse stress (DrC) has been calculated according to: $DE = 100[(E_{LDPE/silica} - E_{LDPE})/E_{LDPE}]$, where $E_{LDPE/silica}$ is the elastic modulus of each type of nanocomposite and E_{LDPE} is the elastic modulus of the neat LDPE and $DrC = 100[(\sigma_{c-LDPE/silica} - \sigma_{c-LDPE})/\sigma_{c-LDPE}]$, where $\sigma_{c-LDPE/silica}$ is the collapse stress of each type of nanocomposite and σ_{c-LDPE} is the collapse stress of the neat LDPE. The results are presented in Fig. 7a and b.

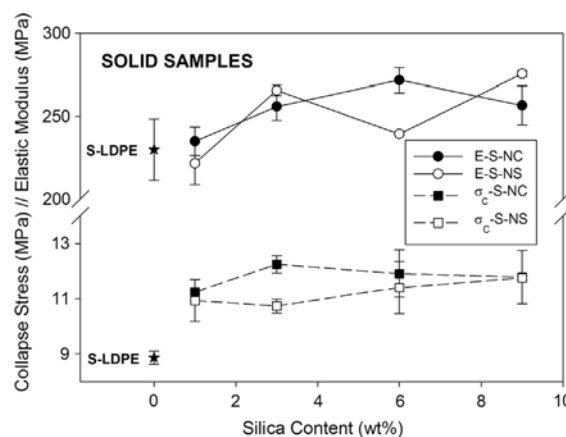


Fig. 6. Experimental results from compression tests for solid LDPE/silica nanocomposites.

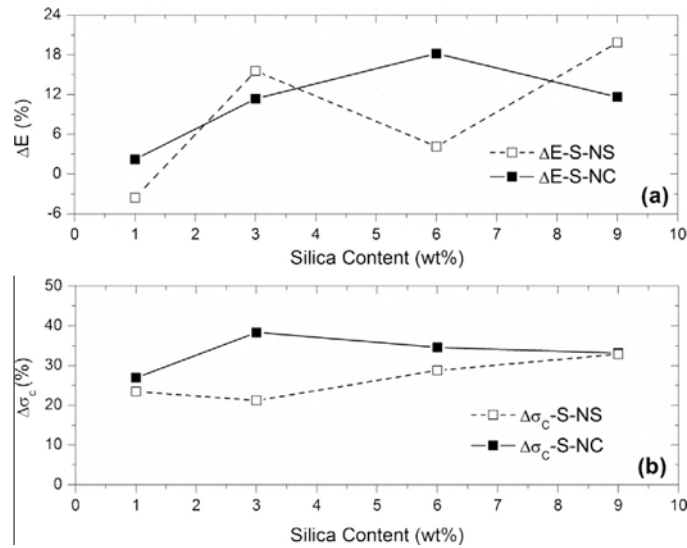


Fig. 7. Improvements, with respect to the pure LDPE, in elastic modulus (a) and collapse stress (b) for solid LDPE/silica nanocomposites with and without compatibilizer.

The first fact that can be inferred from Fig. 7 is that silica particles lead to greater improvements in terms of strength than in terms of stiffness.

In the samples produced with the compatibilizer, a content of silica particles of 6 wt% maximizes the stiffness while for maximizing the strength just a 3 wt% is required. On the other hand, when there is no compatibilizer in the composition of the samples, the optimum silica content to maximize both stiffness and strength is 9 wt%.

While no differences are obtained in the elastic modulus between the samples with and without compatibilizer, the samples with compatibilizer present a collapse stress higher than the samples without compatibilizer, for all the clay contents. After the analysis of the microstructure of the solid samples it was concluded that the differences in the dispersion level achieved for both types of samples were negligible. On the other hand, the analysis of the nucleation effectiveness of the silica particles showed that presence of the compatibilizer led to a higher degree of bonding between LDPE and silica nanoparticles. Results of mechanical response seem to indicate that, for the same dispersion level, the presence of the compatibilizer leads to a better adhesion between the nanoparticles and the polymer. As a consequence a more effective stress transfer is obtained, which results in a slight improvement of the mechanical properties, mainly of the collapse stress.

3.2.2. Mechanical properties of foamed composites

Experimental results corresponding to the characterization of mechanical properties of foams are plotted in Fig. 8.

In general, foamed nanocomposites exhibit higher values of elastic modulus and collapse stress than the pure LDPE. For the foamed composites it has been performed the same type of analysis as for the solid ones. The improvements in the mechanical performance, with respect to the pure LDPE, obtained through the addition of silica particles have been calculated. In addition, the presence of synergistic effects in the foamed materials resulting from the changes produced in both the cellular structure and the solid polymer matrix, by the addition of silica particles, have been carefully analyzed. For this purpose, the improvements achieved in the solid composites, with respect to pure LDPE, are compared with those obtained in the foamed composites. Results corresponding to the increments reached in elastic modulus are presented in Fig. 9.

When the samples include a compatibilizer agent in their composition (Fig. 9a), similar improvements in stiffness for foams and for solids are obtained up to a silica content of 3 wt%. Then, at higher concentrations, the gain in the solids is higher than that observed in the foams. That means that in samples with compatibilizer the changes produced in the cellular structure, by the fact of adding nanoparticles, are leading to a reduction in the elastic modulus, when compared with the improvements achieved in the solid composites. In these foamed composites the optimum silica content, which allows obtaining the maximum improvements in elastic modulus, lies between 3 and 6 wt%.

On the other hand, when samples do not include a compatibilizer in their chemical composition, the improvements reached through the addition of silica particles are generally higher in the foamed composites than in the solid ones, being the optimum silica content 3 wt% (Fig. 9b). In this system, the changes produced in the cellular structure have a positive effect on the overall elastic modulus of the foamed composites. In other words, the presence of a synergistic effect in the foamed materials resulting from the changes produced in both the cellular structure and the solid polymer matrix, by the addition of silica particles, has been detected.

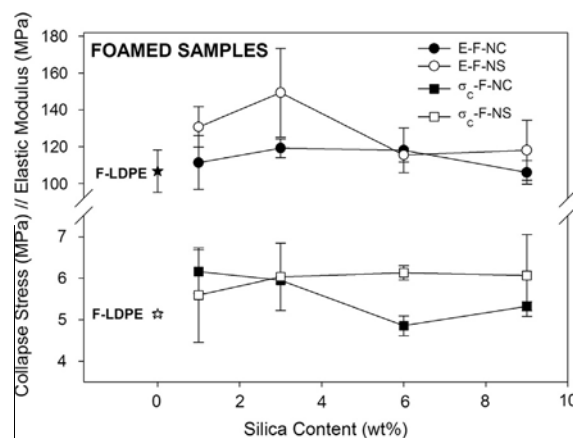


Fig. 8. Experimental results for elastic modulus and collapse stress for foamed nanocomposites with and without compatibilizer.

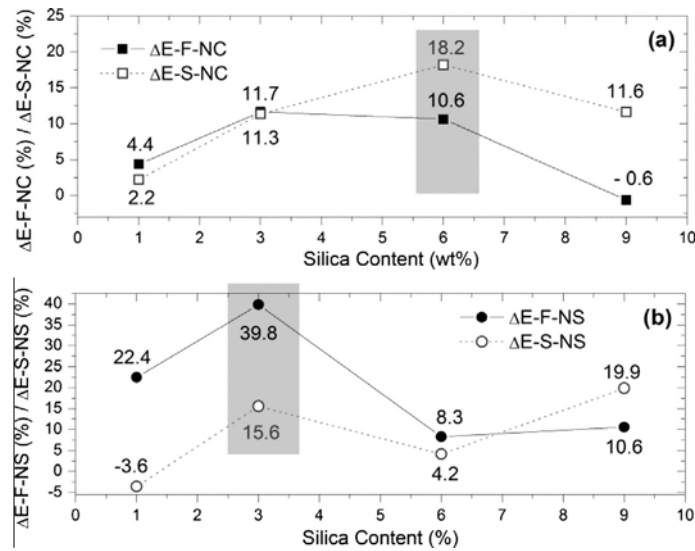


Fig. 9. Increments reached in the elastic modulus of both foamed and solid composites. Elastic modulus for foams (F) and solids (S) with compatibilizer (a) and elastic modulus for foams (F) and solids (S) without compatibilizer (b).

When the improvements achieved in the foamed samples with and without compatibilizer are compared, it is observed that the overall increments in elastic modulus are higher in the foams without compatibilizer.

The gain in stiffness for foams without compatibilizer is a consequence of the improved cellular structure in terms of cell size and cell density exhibited by these materials.

On the other hand, the improvements achieved in the collapse stress have also been analyzed. Results corresponding to the increments reached in the collapse stress for samples with and without compatibilizer are presented in Fig. 10.

In terms of strength (Fig. 10), the gain reached in foams is always lower than that achieved in the solid composites. On the other hand, to accomplish an improvement in foam collapse stress of around 19%, a silica content of 1 wt% is required in the samples with compatibilizer and silica contents higher than 3 wt% are required in the samples without it. Furthermore, while in the solid composites the overall increments were higher in the samples with compatibilizer than in the samples without it, in the foamed composites this behavior is completely opposite. Foamed composites without compatibilizer in their chemical composition present higher increments in collapse stress than the samples that contains the compatibilizer agent. The gain in strength is, once again, a consequence of the improved cellular structure in terms of cell size and cell density exhibited by the materials without compatibilizer.

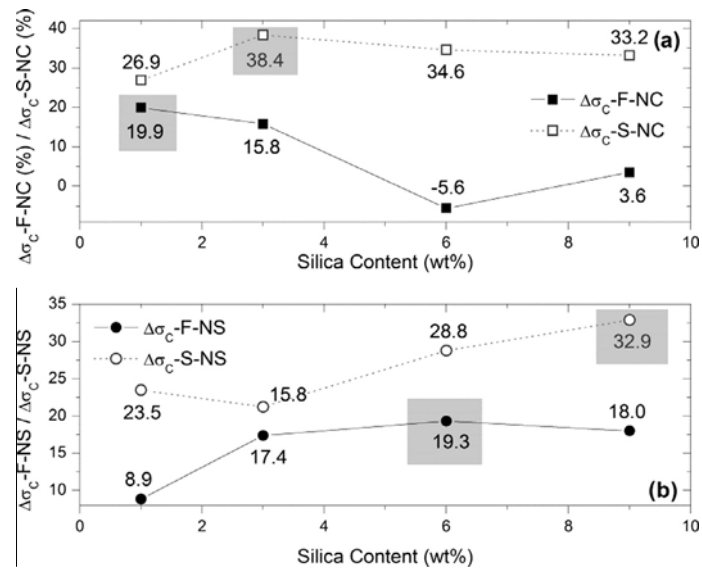


Fig. 10. Increments reached in the collapse stress of both foamed and solid composites. Collapse stress for foams (F) and solids (S) with compatibilizer (a) and collapse stress for foams (F) and solids (S) without compatibilizer (b).

4. Conclusions

LDPE/silica solid nanocomposites with and without compatibilizer have been prepared by melt-mixing. In addition, they have been successfully foamed by a modified version of the pressure quench method using CO₂ as blowing agent.

The role played by silica nanoparticles in solid and foamed nanocomposites has been analyzed at micro and macrostructural levels concluding the following.

In solid nanocomposites, silica particles are not individually dispersed. They are forming aggregates with a size between 100 and 200 nm. In addition, the results for the Agglomeration Ratio indicate that the presence of the compatibilizer does not contribute to increase the dispersion level of the nanoparticles.

Silica particles act as effective nucleating agents as results for cell size and cell density indicate. The effectiveness of silica particles as nucleating agents is greater in the samples without compatibilizer due to the poor adhesion that exists between the polymer and the nanofiller. The presence of the compatibilizer enhances the bonding degree between the two phases and hence, nucleating effect of the particles is mitigated.

Mechanical properties of solid and foamed nanocomposites have been analyzed by performing compression tests. Results indicate that silica particles lead to an overall increase in mechanical response of all the analyzed samples, with respect to the mechanical properties of the pure LDPE.

The improvements in mechanical properties achieved in solids are always greater than that obtained in foams, except in the case of elastic modulus of samples without compatibilizer, which indicates the presence of a synergistic effect. The

synergistic effect is reached due to the multifunctional role played by nanoparticles, which act both modifying the polymeric matrix morphology and the cellular structure of the foams.

Finally, results indicate that the effect of adding or not a compatibilizer agent is not the same in the solid composites as in the foamed ones. While for solid nanocomposites the higher degree of bonding polymer/nanoparticle promoted by the presence of the compatibilizer translates into a positive mechanical reinforcing effect, for foamed nanocomposites, such high level of compatibilization mitigates the nucleating effect of the nanoparticles. This translates into poorer mechanical properties in the foamed samples containing the compatibilizer agent.

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