Electrical properties of nanostructured polypropylene: a matter of morphology?

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ABSTRACT

This work investigates an alternative view on the mechanisms behind the modification of electrical properties in a filled dielectric, based on the variation of morphological properties of materials.

The case of a nanostructured polypropylene-based blend will be analysed, highlighting the morphological changes observed in the bulk of the material with modifications of electrical properties such as space charge accumulation, dielectric strength and conductivity.

Results show that nanofillers help inducing an enhanced morphology of the bulk material, with a reduction of phase separation. This in turn results in better breakdown voltage and lower conductivity, but also an increase in space charge accumulation characteristics to unacceptable levels.

On the other hand, functionalization of nanoparticles has been proven to be able to reduce charge accumulation to levels lower than the neat base material, despite a similar polymeric morphology. This must be due to the improved filler dispersion observed, clearly showing the added value carried by nanostructuring.

KEYWORDS

Insulation, Morphology, Nanofiller.

INTRODUCTION

Nanostructured dielectrics are a fascinating technological solution since their first proposal by Lewis in 1994. The modification of trap density and depth by nanoparticles and their surface functionalization affects several electrical properties in ways that are hard to control or predict [1],[2]. Space charge accumulation, breakdown properties and conductivity are only some of the several properties potentially modified by nanofillers.

Tailoring a material with selected improved characteristics should be possible by carefully selecting fillers with an adequate nature and dispersion [3] but hard to achieve in a cost-effective way, given the high level of precision and control this production would require.

Polymers featuring certain characteristics can be interpreted under a certain level or ordering of its micro and macroscopic structure. The structure that forms during polymerization critically defines the properties of the final material, and having, for example, the right range of molecular length is crucial for achieving thermomechanical integrity with the desired properties of thermoplasticity and rheological characteristics of a product.

Other works experimented the possibility to achieve enhanced properties through blending, after the addition of different grades of polymers, with good results [4],[5].

An alternative way of providing materials with improved characteristics might come from the modification of internal morphology that fillers introduce during the polymerization processes [6].

CRYSTALLIZATION PRINCIPLES

Among the possible levels of order a polymer can exist, crystallinity is the most important concept, as with metals.

The two factors mainly influencing the physical properties of solid polymers, once the basic chemical composition of chains is selected, are defects and the set of parameters chosen during the crystallization stage. This work will focus on the first aspect.

All polymers have defects, to some extent. The most common type of defect comes from the geometrical placement of moieties within the monomer along the polymer backbone, differentiating three possible structures of a polymer: isotactit, syndiotactic, and atactic.

Branches, impurities in the structure, end of chains and inclusions are considered defects. Those irregularities deeply influence how a polymer will be able to solidify. Indeed, from a thermodynamic point of view, the Gibbs Thomson equation (Equation 1) links the melting temperature T_m with enthalpy of melting ΔH_v, surface free energy σ_e, and crystal dimensions l. T_m^0 is the temperature at which infinitely large crystals will melt.

$$T_m = T_m^0 \left(1 - \frac{2\sigma_e}{l\,\Delta H_v}\right) \qquad (1)$$

Since crystals always start growing from secondary nucleation, starting from a defective site in the melt, crystal dimensions will also be limited by the presence of defects. In other words, the theoretical dimension of a crystal, l, is limited in practice by the distance between nucleation sites (i.e. defects). A high concentration of defective molecular structures will result in a final morphology characterized by smaller crystals, in turn decreasing the temperature that they form at.

Therefore, it is possible to gather a lot of control over the way crystallization occurs when control over defective regions is also allowed (e.g. purposefully introducing a certain concentration of irregularities).

It must be said that this opportunity is always limited by the fact that polymers are statistical entities (molecular length or defect size and concentration is not a constant but rather a distribution of values). The statistical process of polymerization is then not always perfectly defined *a priori*.

INCLUSION OF ADDITIVES: MORPHOLOGICAL EFFECTS

The theory of Keith and Padden [7] indicates that a high concentration of weak and defective material is found in boundaries after crystallization, and therefore, when large structures are formed, bigger highly defective regions will also be formed in the solid. Those are the regions that will most likely cause a mechanical or electrically failure.
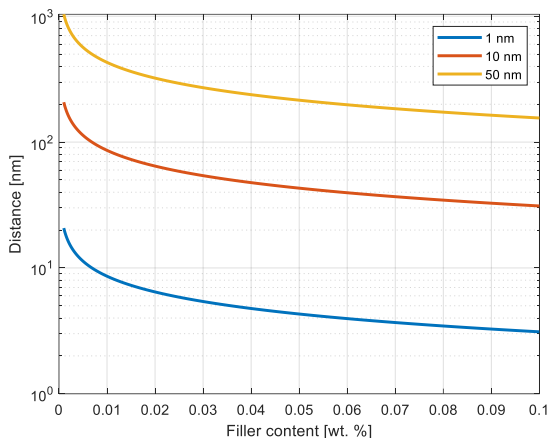
Fig. 1. Average distance between filler particles, calculated according to (1), for $\rho_f = 2650 \ kg/m^3$, $\rho_m = 946 \ kg/m^3$, and different radii.

Phase separation at dimensions above the nano-scale and the formation of weak boundary regions both have detrimental electrical consequences.

It is possible to overcome this by reducing the size of crystals through the inclusion of additives, and engineering materials without conventional boundaries. This can be achieved purposefully introducing an external source of irregularities.

This principle was exploited in the past [4],[5] by means of the addition of both foreign copolymers and particles, acting as additional nucleating sites. Those works reported successful results, usually referring to dielectric strength properties.

In this paper, silica nanoparticles will be considered and a more extensive investigation on electrical properties will be carried out. Considering an ideal melt, with spherical SiO_2 particles having a constant radius, r, uniformly dispersed in a homogeneous and isotropic polymeric matrix, the average distance among the particles, d, can be obtained by [3]:

$$d = r \left\{ \left[\frac{4\pi}{3} \left(1 + \frac{1-F}{F} \frac{\rho_f}{\rho_m} \right) \right]^{\frac{1}{3}} - 2 \right\} \qquad (2)$$

where F is the filler concentration (wt. %), ρ_f and ρ_m are filler and matrix densities. Figure 1 shows the case of a SiO_2 filler in a Polypropylene matrix, for different filler size. This will physically constitute an upper value for the crystal size, l.

It can be noticed that smaller particle size always results in smaller distances. Increasing the filler percentage also contributes to this reduction, but it should also be taken into account the increasingly high risk of agglomeration of those particles. In practice, it is not necessary to achieve high level of filler content, since already increasing the filler content from 1 to 5% the actual distance is decreased by only 50%. For this work, a commercially available filler average diameter of 25 nm and percentage of 1% was

considered, corresponding to a maximum theoretical value of $l = 214 \ nm$.

MATERIALS AND METHODS

Two different blends of polypropylene and elastomers were filled with a 1%$_{wt.}$ of SiO_2. The base random copolymers will be here called A and B, and differ by their main structure being more or less heterophasic respectively. In order to improve the dispersion of the filler into the matrix and reduce the issue of agglomeration, silica nanoparticles were subjected to a functionalization treatment using a silane, dried for 48h in a vacuum oven at 80 °C.

Scanning Electron Microscope (SEM) pictures were taken before and after filling the base materials, and their electric performance was evaluated by means of dielectric strength, conductivity and space charge accumulation measurements. Measurements were performed on thermally pre-treated specimens (72 hours at 60° C in vacuum). This is done to remove traces of water diffused into the material.

Dielectric strength was measured at room temperature by ramp-voltage tests in oil, using cylindrical rods with 6.4 mm of diameter with edges rounded to 0.8 mm radius (ASTM D3755) as electrodes. Conductivity was measured using a Keythley B2980 electrometer and waiting for the stabilization of polarization current under a constant field of 50 kV/mm and 60 °C of temperature.

Space charge measurements were carried out by the Pulsed Electro-Acoustic (PEA) method. This is a fundamental parameter for the characterization of insulating material for DC applications, because the presence of space charge in the insulation can modify substantially the electric field distribution and, hence, the insulation life. Measurements during 3-hour polarization (while DC voltage is applied) and depolarization (while DC voltage is absent) times are carried out in this work. Tests are done at 60°C, in controlled environment, applying a constant 50 kV/mm field.

Apparent trap-controlled mobility is a rough approximation of the mobility as usually defined, but, even if affected by significant approximation, can be useful for material characterization and aging diagnosis. The expression of apparent trap-controlled mobility is the following [8]:

$$\mu(t) = \frac{\varepsilon}{q^2(t)} \frac{dq(t)}{dt} \qquad (3)$$

where L is specimen thickness, $q(t)$ is the charge density that can be calculated at any depolarization time, $dq(t)/dt$ is the slope of the depolarization curve at time t, ε is the permittivity of the specimens tested. The values for apparent mobility was evaluated during the first seconds of depolarization, corresponding to the highest level of charge mobility allowable in the polymer.

As previously said, this work will focus only on the effect of nanofillers on morphology, while keeping constant other important factors as cooling profiles and extrusion speeds, not considered here.

Table 1 – Results of the electrical characterization of tested materials. Standard errors in square brackets.

Material name	Dielectric strength [kV/mm]	Conductivity [S/m]	Space charge [C/m^3]	Apparent mobility [m^2/Vs]
A	467 [8]	$1.7 \cdot 10^{-14}$	0.6 [0.05]	$3 \cdot 10^{-12}$
A$_{1\%}$	472 [14]	$5.7 \cdot 10^{-15}$	1.51 [0.22]	$1.7 \cdot 10^{-13}$
A$_{1\%\_f}$	496 [14]	$7.8 \cdot 10^{-15}$	0.39 [0.02]	$1 \cdot 10^{-12}$
B	364 [18]	$1 \cdot 10^{-14}$	0.55 [0.04]	$1.5 \cdot 10^{-12}$
B$_{1\%}$	398 [5]	$9.6 \cdot 10^{-16}$	0.95 [0.07]	$1.4 \cdot 10^{-13}$
B$_{1\%\_f}$	435 [7]	$2.5 \cdot 10^{-15}$	0.58 [0.03]	$4 \cdot 10^{-13}$
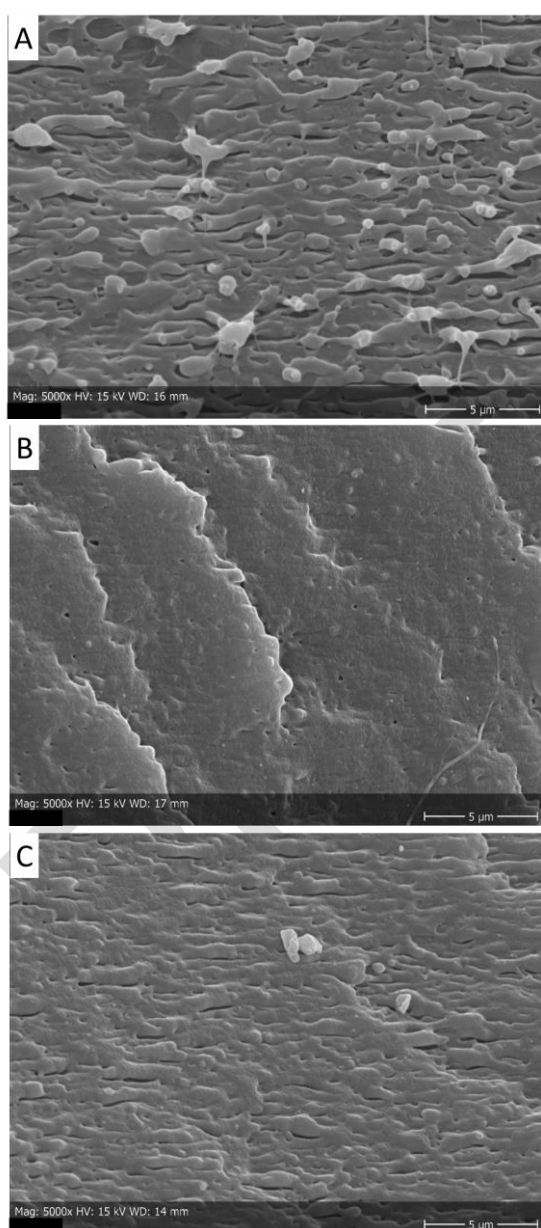
Fig. 2. SEM pictures for the material A. A: neat copolymer, B: material filled with 1%$_{wt.}$ Of untreated SiO$_2$ nanoparticles, C: material filled with 1%$_{wt.}$ of SiO$_2$ nanoparticles treated with silane.

RESULTS AND DISCUSSION

Let us analyze the SEM images for material A, in Figure 2. It can be noticed that the neat, non-filled copolymer A is characterized by a particularly inhomogeneous structure (Figure 2A). This is due to the heterophasic nature of the blend. Adding a small percentage of nanofiller contributes to a strong modification of the morphology, and a much more homogenous structure is obtained (Figure 2B).

This is reflected on the results coming from the electrical characterization (Table 1). Breakdown field for the nanofilled material has a mild increase from the original value of 467 kV/mm for the neat blend, to 472 kV/mm. Conductivity is substantially reduced from $1.7 \cdot 10^{-14} \, S/m$ to $5.7 \cdot 10^{-15} \, S/m$. This is beneficial for HVDC applications, especially in the case of defective materials prone to PD inception under steady state conditions, which are able to quickly deteriorate materials and reduce life [9].

Those two improvements can be directly linked to the reduction of the average dimension of highly defective and conductive regions, through which breakdown can occur and conduction paths develop. While the neat material shows highly coarse structures, its nano-filled counterpart features a more refined, less granular morphology. This means that physically bigger defective regions have to be expected in the first case, while the same amount of interfacial defective volumes is scattered in a more dispersed manner, contributing to the reduction of failure patterns. Indeed, mobility of charges is reduced from an estimated value of $3 \cdot 10^{-12}$ to $1.7 \cdot 10^{-13} \, m^2/Vs$.

On the other hand, a side effect of nanofilling is the increased space charge accumulation, going from the original value of $0.6 \, C/m^3$ to $1.51 \, C/m^3$. This aspect can be related to an improper dispersion of the filler, and should be improved when a functional layer with the purpose of reducing agglomeration of particles is added to its surface.

As can be seen in Figure 2C, after the addition of a silane the morphology of the surface tends to recover some roughness, still maintaining lower levels from the original material. As a consequence, conductivity and mobility of charges have values in between the neat and filled materials: $7.8 \cdot 10^{-15} \, S/m$ and $1 \cdot 10^{-12} \, m^2/Vs$.

Space charge accumulation has a major reduction, reaching $0.39 \, C/m^3$, a value even lower than the neat polymer. The reduction of space charge accumulation is

possibly the reason for the mild improvement of dielectric strength, which is further increased to 496 kV/mm (+6% from the original value).

Figure 3 shows SEM images for material B. This second base material is characterized by a more homogeneous structure (Figure 3A) from the beginning. The addition of 1%$_{wt.}$ of nanofiller further reduces the granularity of morphology (Figure 3B). Results from the electrical characterization (Table 1) are consistent with what was previously said. The dielectric strength of the nanofilled material has an increase from 364 kV/mm for the neat blend, to 398 kV/mm, while conductivity is reduced from $10^{-14}\ S/m$ to $9.6 \cdot 10^{-16}\ S/m$. Apparent mobility of charges is also lowered from an estimated value of $1.5 \cdot 10^{-12}$ to $1.4 \cdot 10^{-13}\ m^2/Vs$.
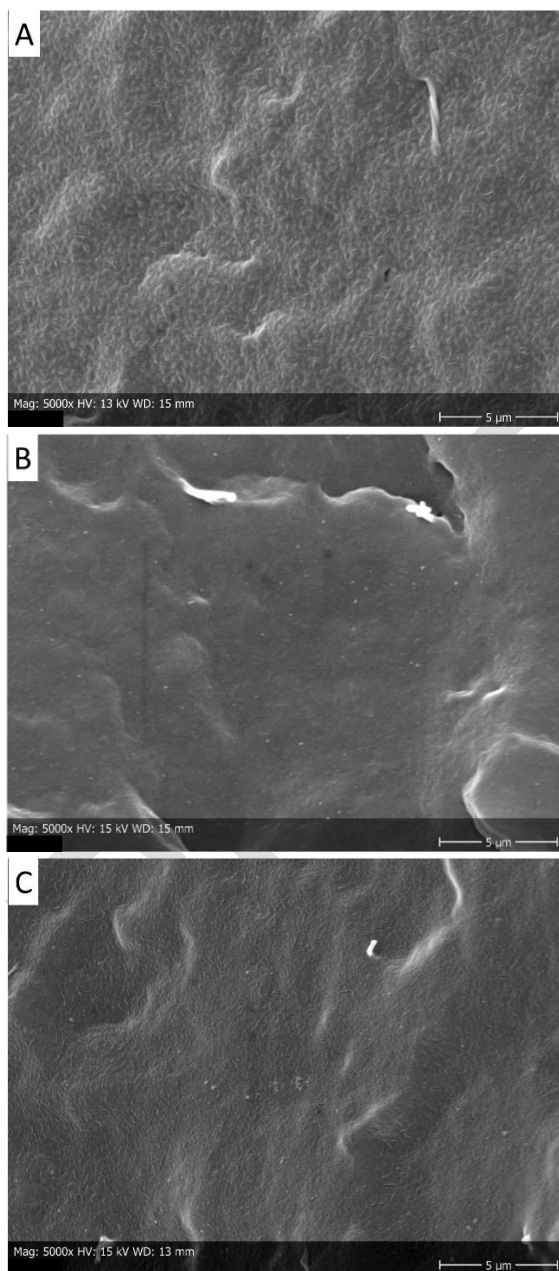
Fig. 3. SEM pictures for the material B. A: neat copolymer, B: material filled with 1%$_{wt.}$ of SiO$_2$ nanoparticles, C: material filled with 1%$_{wt.}$ of SiO$_2$ nanoparticles treated with a silane.

As before, a small increase in space charge accumulation is observed, going from the original value of $0.55\ C/m^3$ to $0.95\ C/m^3$.

After the addition of a functional group, as can be seen in Figure 3C, the morphology of the surface appears to regain some inhomogeneity, as in the previous case, while conductivity and mobility of charges have a value in between the ones for the neat and the filled material: $2.5 \cdot 10^{-15}\ S/m$ and $4 \cdot 10^{-13}\ m^2/Vs$.

Space charge accumulation is reduced to $0.58\ C/m^3$, a value in line with the neat polymer. Even in this case, the dielectric strength is further increased to 435 kV/mm (+20% from the original value).

CONCLUSIONS

This paper reports the progress in the development of a nanocomposite insulation material based on Polypropylene. The effect of nanofillers on morphological aspects and the resulting changes in dielectric performance were investigated and discussed.

Inhomogeneous structures rising from the development of crystalline structures, or heterophasic topologies such as those shown in Figure 2A and 3A contributes to decrease the life of a material, introducing undesired regions where both mechanical and electrical stress might be enhanced.

Adding SiO$_2$ nanoparticles in a base polymer may be effective to induce morphological changes to the microscopic structure of the polymer, improving the electrical properties of the resulting product.

The burden of agglomeration can cause unwanted effects, such as higher space charge accumulation and shorter life of materials under a constant electric stress [10]. This can be mitigated by the surface functionalization of nanostructured materials, but further work is currently in progress in order to improve this aspect and eventually fully exploit the high potential of those composite polymers.

ACKNOWLEDGMENT

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