Improved impact toughness PVC composite with surface modified nano calcium carbonate, obtained by a novel physicochemical top-down manufacturing process

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ABSTRACT

A novel top-down process was developed for produce surface modified calcium carbonate nanoparticles (NCC), 40 nm average size particles were functionalized in a water suspension by using energy from top-down physicochemical process. Well dry coated nanoparticles were mixed by a high speed mixer with PVC resin, optimum concentration of NCC was determined by experimental design to reach the best impact strength, reducing normal concentrations of processing aid and impact modifier of PVC formulation. Extruded PVC composite was analyzed by izod impact testing. Mechanical properties testing of PVC nanocomposite, demonstrate that NCC can affect positively tensile strength. Scanning electron microscopy images showed homogeneous dispersion of nanoparticles in polymer matrix, and improved ductility. Impact strength control values were increased up to 50% reducing normal impact modifier concentration from 6 to 4 phr.

Keywords: calcium carbonate nanoparticles (NCC), PVC, impact strengh, extruder.

1 INTRODUCTION

The use of impact modifiers due to the need to extend the lifetime of avoiding PVC materials faults and fractures, increasing its strength and preventing fractures losses during transportation, storage, distribution, installation and operation[1,2,3].

The impact strength is a weak point in the spectrum of properties of some polymers. Special cases such as PP, PS and PVC have inherently poor impact resistance at low temperatures mainly, limiting its application and use [4,5,6,7]. To this formulation used, including impact modifiers.

The use of nanoparticles for this purpose has proved to be an alternative that provides promising results, allowing for increased toughness of the material without necessarily modifying the tensile strength [6,7,8,9,10], inclusion of ceramic nanoparticles with or without functionalized as PVC matrices can increase the tenacity of based on characteristics such as particle size, inclusion process, the presence of impact modifiers and finally the material, the type and degree of functionalization.

Nanometric calcium carbonate induces substantial improvements in the material [6,7], such as impact resistance improvement without altering Young's modulus and can modify the flow properties, which is also used as a processing aid (molecular lubricant). Also has a greater dimensional stability, the Vicat temperature increases and improves the dielectric properties.

According to the functionalization nanometer $CaCO_3$ particles can: Grouping, flowing, sediment, broken, or agglomerate. It can also serve as seeds for the formation of crystalline regions.

The improvements depend on the material:

- Distribution.
- Dispersion.
- Morphology of the system before / during / after extrusion.
- More surface area of the particle.
- Interactions between the particle and the polymer matrix.

While the factors affecting the performance of impact modifiers and should be considered are [6,7]:

- Evolution of morphology during the production process.
- Fusion of secondary particles of PVC (50 to 200um) (gelation of PVC).
- Formation of an elastomeric network.
- Training of immiscible phases.
- Factors affecting the morphology of the system.
- Concentration of nanoparticles.
- Interaction (compatibility) between nanoparticle / PVC.

PVC impact resistance is improved by adding small amounts of nano calcium carbonate, in this work we developed a novel manufacturing process to obtain an effective nano impact modifier based on functionalized nano calcium carbonate [6].

2 EXPERIMENTAL

All chemicals were purchased as standard grade without purification in order to study an scalable process.

Micronized precipitated calcium carbonate, chemical dispersant, stearic acid and deionized water was added in a milling process in appropiate concentrations.

Production of nanoparticles was performed by a physico-chemical process of grinding by top-down method, using a blasting material to reduce the particle size. Apropiate dispersants are added to the suspension in order to achieve a good dispersion and minimize particle size.

Particle size can be reduced from some microns to 40 nanometers.

Functionalized 40 nm average size nanoparticles was obtained, this particles are totally compatible with the polymer matrix due to its functionalization. For remove water of emulsion, it was centrifuged, dried, crushed and screened for to obtain a powder of functionalized nano calcium carbonate on a dry basis. The nanocomposite was integrated by high speed mixing with the PVC resin before being processed by an extrusion process.

This novel method allows to get particles than can be dispersed in the polymer matrix by one step (milling-functionlizing) process.

3 RESULTS

Nanocalcium carbonate particles was characterized for to obtain their size, morphology, cristalinity, and functionalization degree. Mechanical properties are improved significantly, impact resistance can be improved even reducing impact modifier up to 50%.

3.1 Particle size

Initially calcium carbonate particles are mainly bigger than 1 micron size, in the Fig. 1 a) ,b) and c), a secuence of TEM images show the reduction of particle size in different moments of grinding process, final particle size was achieve when average particle size is 40 nm measured by DLS technique.

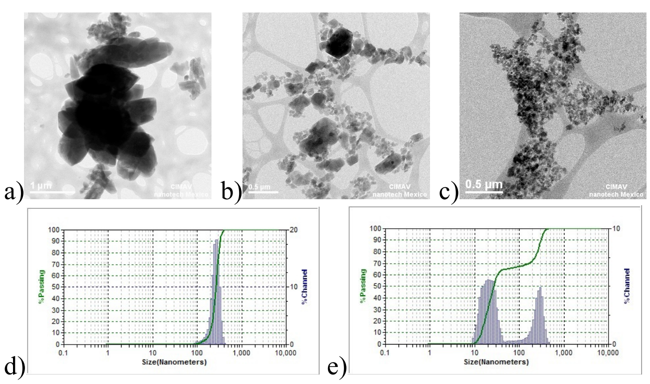

Figure 1. Evidence of size reduction of calcium carbonate by milling process. a) TEM image of raw $CaCO_3$, b) intermediate product with some nanometric particles, c) final product, 40 nm size particles, d) DLS result of measured raw suspension, e) nanocalcium carbonate bimodal sample.

3.2 X-Ray Difraction

X ray diffractogram Fig. 2 corresponds to grinded calcium carbonate (calcite), this result shows absence of another crystalline phase.

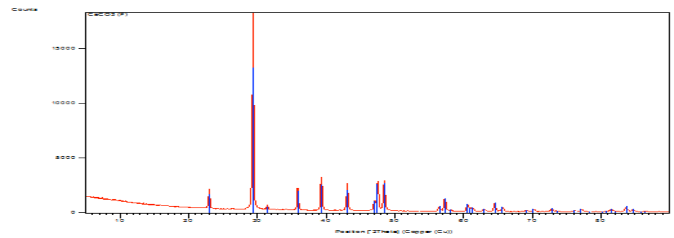

Figure 2. X-ray pattern, corresponding to calcium carbonate (calcite).

3.3 FTIR

Presence of organic functionalizing agents was performed by FTIR, a measurement of the transmission spectrum of the electromagnetic field in the region of a medium infrared FTIR was performed. In the Fig. 3, NCC unfunctionalized spectrum and absorption bands due to the functionalizing agent in the particles is observed.

Bands in 2700-3000 cm^{-1} region, corresponds to the absorbance vibrational phenomena of links associated with aliphatic chains of functionalizing elements.

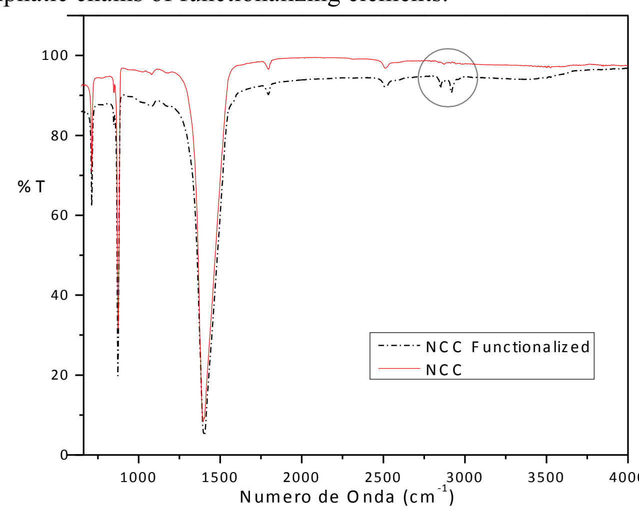

Figure 3. FTIR NCC spectrum unfunctionalized $CaCO_3$ and Funcionalized $CaCO_3$ with stearic acid.

3.4 SEM

SEM image in Figure 4, show nano calcium carbonate particles, particles are shown together in a powder sample, this aggregate can be deaglomerate by a high mixing process. SEM image show narrow size distribution.

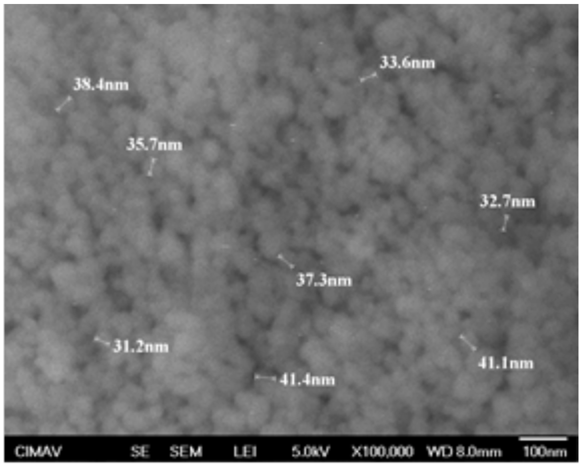

Figure 4 SEM image of NCC functionalized

3.5 TEM

In the image of transmission electron microscopy can be observed in more detail the cubic shape functionalized NCC, with sizes between 20 to 70 nm.

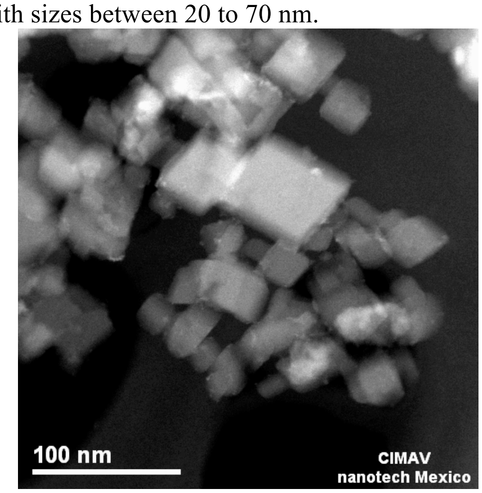

Figure 5. TEM image of NCC functionalized

This section describes the results for the nanocomposite comprises nanoparticles and calcium carbonate are presented PVC resin

3.6 Mechanical Properties

This section describes the results for the nanocomposite comprises calcium carbonate nanoparticles in the PVC composite.

PVC nanocomposite was formulated using different concentrations of nanocalcium carbonate, but also different impact modifier concentrations. This samples was compared with standard sample with standard concentration of impact modifier. Additional sample was introduced in this analysis, PVC REF correspond to a sample with a reduced concentration of impact modifier (IM), in order to compare with NCC samples at the same concentration of IM.

Fracture analysis using SEM was performed in PVC nanocomposite sample. The results show that nanoparticles where correctly dispersed in polimer matrix, in figure 6, arrows indicate the position of some nanoparticles, who mainly are found in top edge of fracture material displacement. Nanoparticles improves ductility of composite, incresing impact toughness.

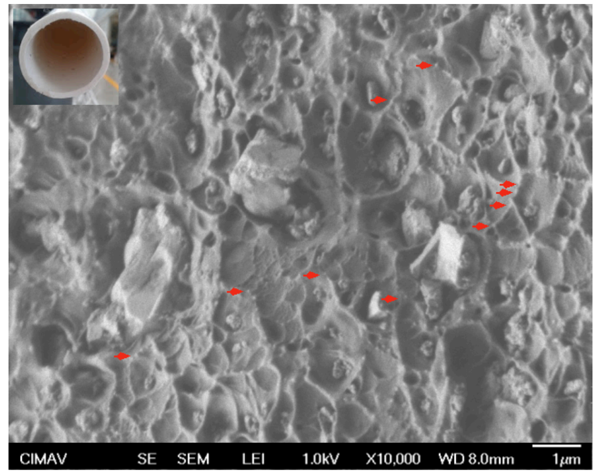

Figure 6. SEM image of fracture edge of PVC nanocomposite, obtained by cryogenic rupture. Nanocomposite PVC pipe section (Top left).

Standard composition of PVC composite has 6 phr of impact modifier, samples was analyzed decreasing IM to 4 and 2 phr, using 3.5 and 7 phr of NCC, low and high concentration of nano additive respectively.

Using high concentration of NCC and IM, maximum impact toughness was reached, increasing from 100.8 J/m to 153.3 J/m this is 52% of increase of impact resistence, 1.5 times the standard resistance.

Reducing IM concentration to 2 phr, is posible to increase impact resistance even at low concentration of NCC, this result shows that by using NCC even at 3.5 phr, impact resistance is increased from 100 to 108 J/m, reducing the cost of production of PVC composite, because the lower cost of NCC compared with IM and the lower concentration that it needs.

Table 1 shows the results of impact resistance for each sample, PVC REF sample shows an important reduction of impact resistance, this reference confirm that NCC are increasing impact toughness of PVC composite.

Table 1. Mechanical properties of PVC composites.

ID	NCC Conc. (phr)	IM Conc. (phr)	Impact Resistance (J/m)	Tensile strength (Mpa)	Rupt. elongation (%)
PVC STD	0	6	100.8	42.33	119.2
PVC REF	0	2	69.7	45.48	114.7
PVCNCC1	3.5	4	112.9	39.37	101.7
PVCNCC2	3.5	2	108.2	39.58	105.6
PVCNCC3	7	4	153.3	40.41	100.5
PVCNCC4	7	2	114.5	39.30	117.9

Mechanical properties were completed with tensile resistance, tensile stregth of nanoformulated samples decrease slightly meanwhile elongation in rupture remains at a similar value. These results show that NCC increase ductility of PVC composites.

4 CONCLUSIONS

Calcium carbonate particle size, can be reduced from 1 micron to 40 nm in a water suspension.

Functionalized NCC obtained by one step physicochemical process, is an additive that can increase impact resistance up to 1.5 times.

NCC additive increase ductility of PVC composite even at low concentrations (3.5 phr).

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