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Monitoring migration and transformation of nanomaterials in polymeric composites during accelerated aging

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Monitoring migration and transformation of nanomaterials in polymeric composites during accelerated aging

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Abstract. The incorporation of small amounts of nanoadditives in polymeric compounds can introduce new mechanical, physical, electrical, magnetic, thermal and/or optical properties. The properties of these advanced materials have enabled new applications in several industrial sectors (electronics, automotive, textile...). In particular, for the nanomaterials (NM) described in this work, multi-walled carbon nanotubes (MWCNT) and silicon dioxide nanoparticles (SiO_2 NP), the following properties have been described: MWCNT act as nucleating agents in thermoplastics, and change viscosity, affecting dispersion, orientation, and therefore mechanical, thermal, and electrical properties; and SiO_2 NP act as flame retardant and display improved electrical and mechanical properties.

The work described here is focused on the evaluation of the migration and transformation of NM included in polymer nanocomposites (NC) during accelerated climatic ageing. To this aim, we generated polyamide 6 (PA6) NC with different degree of compatibility between the NM and the polymeric matrix. These NC were submitted to accelerated aging conditions to simulate outdoor conditions (simulation of the use phase of the polymeric NC). The NC contain as nanofillers MWCNT and SiO_2 NP with different surface properties to influence the compatibility with the polymeric matrix. The generated NC were evaluated by scanning electron microscopy (SEM), transmission electron microscopy (TEM) with Energy-dispersive X-ray spectroscopy (EDX), thermogravimetry (TGA) and differential scanning calorimetry (DSC) before and after the aging process, to monitor the compatibility of the NM with the matrix: dispersion within the matrix, migration during aging, and modification of the polymer properties.

The dispersion of SiO_2 NP in the NC depended on their compatibility with the matrix. However, independently of their compatibility with the matrix, SiO_2 NP were aggregated at the end of the accelerated aging process. In addition, degradation of the matrix and migration of nanoparticles to the surface was observed as well in the different types of SiO_2 NP aged NC. Oppositely, compatibilized MWCNT ($MWCNT_{MB}$) decreased the degradation of the polymer. Nevertheless, the nanomaterial migrated likewise to the surface during the ageing process.

In order to evaluate the possible changes in the structure of nanomaterials due to the aging process, NM were extracted from the polymer by calcination. The nanomaterials extracted were analyzed by TGA, Fourier transform infrared spectroscopy (FT-IR), BET and TEM and its properties compared with calcinated raw NM. SiO_2 hydrophilic nanoparticles were not affected by the aging process. However, both types of MWCNT were affected by the aging of the NC.

1. Introduction

Polymer materials are a growing area in all the industrial sectors because of their properties and ease processing. The addition of small amounts of nanoparticles to polymers leads to new and/or improved properties for these materials such as mechanical, physical, electrical, magnetic, thermal or optical properties. These NC present interesting applications in most of the industrial sectors, in particular in the electronic, automotive, textile and mining sectors.

To assess the potential value of NC, it is important to determine which nanomaterials can be effectively integrated into NC and what new or improved properties this enables. Then, it is important to determine the effectiveness of dispersion of the nanomaterial in the matrix and how this affected the structure of the polymer to enable the desired property. Polyamides are highly used engineering thermoplastic materials due to their good performance /cost balance. Moreover, PA offers interesting chemical and mechanical properties such as rigidity, chemical resistance, abrasion resistance and barrier properties.

The incorporation of the NM inside of polymeric matrix contributes to an improvement of the polymer properties or adding new properties. Nanofillers are only a few nanometers in dimension offering large surface area per volume and novel properties at this scale. The addition of small amounts of these nanofillers leads to NC materials with enhanced or novel properties, which in some cases allows the use of these materials in new sectors. In this work, SiO_2 NP and MWCNT have been selected to generate PA6 polymer NC. SiO_2 NP can offer interesting mechanical and thermal properties such as mechanical resistance, anti scratching and anti abrasion and anti corrosion.[1-2] On the other hand, MWCNT act as nucleating agents [3] leading to new crystallographic morphologies of the polymers which offer enhanced mechanical, thermal and electrical properties compare to the starting material.[4-7]

The improvement of the material properties by the addition of nanofiller is achieved if the interaction between nanomaterials and the matrix is optimal (homogenous dispersion of the nanofiller inside the matrix). The big differences in the properties of polymer and nanomaterials can often cause phase separation, which it could affect the properties of the resulting NC. [8-9]

Several methods have been studied to enhance the compatibility between the polymer and nanomaterial. The most frequently method used to enhance the compatibility between NM and polymer and therefore to improve the dispersion of them in the polymeric matrix is the nanoparticle surface chemical modification.

Regarding SiO_2 NP, chemical surface modification is the most commonly used method. In this case, silane coupling agents were used as surface modifier agents. The general structure of silane coupling can be represented as $RSiX_3$, where X represents the hydrolyzable groups and R corresponds to organo groups with different functional groups which will improve the interaction between SiO_2 NP and polymer. Different polymeric silane coupling agents has been developed such as aminopropyl methydiethoxysilane (APMDES), vinyltriethoxysilane (VTES), dimethyldichlorosilane (DDS), among others. [10-16]

Commonly, carbon nanotubes have been used as reinforcing materials by their incorporation into a polymeric matrix. However, optimal properties are difficult to achieve due to the deficiencies in nanotubes dispersion and alignment. The state of CNT dispersion within the diluted composites is influenced by processing conditions and compatibility between CNT and polymer matrix. It was demonstrated by recent scientific papers that satisfactory carbon nanotubes dispersion can be obtained using different strategies including physical and chemical methods. Physical methods include carbon nanotubes direct mixing using a mechanical force while chemical methods are based on carbon nanotube surface modifications such as surfactant or polymer wrapping technology. [17-18] Master batches, thermoplastic polymers containing high loading of CNTs (15-20%), have recently became widely used in the melt preparation of CNT based polymer NC. For industrial application of melt mixing extrusion technique, the use of master batch materials is preferred to improve CNT dispersibility in the polymer matrix.[19-24] Additionally, master batches offer a dust-free environment and consequently no safety-risk concerns are considered.

Nowadays, different strategies to recycle the NM or NC are being studied because of the added value of the nanofillers. These strategies can be distributed in two big sectors: mechanical and chemical recycling. Mechanical recycling is less destructive method for the recovery and reuse of NM-polymer mixture. However the chemical recycling methods can be very interesting because it is possible to separate the NM from polymeric matrix. The last can be calcinated or dissolved with the corresponding solvent depending on the polymer used.

This work describes the evaluation of the potential release of nanomaterials from polymeric NC during their use in outdoor applications. The importance of NP dispersion and compatibility with the matrix in NC materials are key issues to avoid release of NM to the environment. Size, shape and composition of the nanofillers are found to influence the potential release of SiO_2 NP and MWCNT from PA6 NC.

2. Materials & methods

MWCNT (NC7000, 90% pure) and MWCNT master batches with a 15% of nanofiller content (PLASTICYL^{TM} PA1503) were obtained from Nanocyl^{TM}. Two different types of nanosized SiO_2 were acquired from PlasmaChem to get different degrees of compatibility between NM and polymer: non-modified SiO_2 (hydrophilic; PL-SiOF) and SiO_2-octyl (hydrophobic; PL-SiOF-OS, 99.8% pure).

2.1. Extrusion and Injection of the NC

The polymer used, PA6, is an aliphatic hygroscopic homopolymer. Thus, it was dried with a dehumidifier Wittmann PDC (Portable Drying Conveyor) before extrusion/injection treatment to prevent the hydrolytic degradation and alteration of its properties. To ensure maximum dispersion and homogenization of the NP within the polymeric matrix, first NM were mixed with PA6 and extruded in a co-rotating twin screw extruder (TSE20, Brabender) to obtain a pellet with a 3% of nanofiller content. NC pellets (3% nanofiller content) were injected to obtain standard test specimens in a 100 tons clamping force injection machine (TM110, Battenfeld).

2.2. Accelerated weathering process

In order to study the climate effect on the different NC, accelerated aging was performed in a climatic chamber (Suntest XXL+, Atlas). Conditions chosen were based on ISO 4892/06 (table 1):

Ageing Conditions	
Irradiation (at 300-400 nm):	0.50 W/m^2
Internal filter:	borosilicate
External filter:	borosilicate
BST temperature:	65ºC (±3ºC)
Relative humidity:	50% (±5%)
Wetting/cycle:	1 ± 0.5 min
Drying:	29 min
Irradiation:	continuous
Total exposure:	1000 h

Table 1. Ageing conditions based on ISO 4892/06

After aging, the characterization of all the samples was performed using TGA, FT-IR, DSC, TEM, SEM and EDX techniques.

The weight loss of the samples was analyzed, both qualitatively and quantitatively, by Hi-Res TGA (Q500, TA instruments), applying a temperature increase of 10°C/min from 30-1000°C and a flow rate of air at 50 mL/min. Weight loss 160°C was considered due to hydration of the sample and discarded for analysis. DSC was used to determine melting and crystallization temperatures (T^a_m & T^a_c respectively), glass transitions and the estimation of the crystallization kinetics in each NC injected. mDSC (Q20, TA instruments) with a RCS module was used for these analyses. The conditions selected were temperature programming of 10ºC/min from 30-250ºC, and a flow rate of air at 60mL/min. Functional groups present in the samples were identified using a FT-IR spectrophotometer (IR Affinity-1 8400, Shimadzu). Finally, compatibility between NM and the polymeric host and migration of the nanofiller were determined using SEM (MERLIN FE-SEM, Zeiss) and TEM (Jeol 2010, JEOL Ltd). For TEM microscopy: 2 mm^2 cubes of non-aged and aged specimen tests were cut and included in Epon resin. After resin polymerization (60 °C, 48 h), sections with a thickness of 50 nm were cut with an ultramicrotome and placed on TEM grids (Formvar carbon-coated Cu grids, EMS).EDX in TEM cuts was used to determine the atomic composition of the sample.

2.3. *Calcination process*

The NM were extracted from non aged and aged NC by calcination process. Calcination of the nanomaterial took place at 410 °C for 3h 30 min. The material recovered was characterized by TGA, FT-IR, TEM and EDX.

3. Results & discussion

3.1. *Alteration of the NC properties by the nanofiller nature and compatibility*

It has been widely described that the quality, useful life and properties of the polymers can be significantly modified adding only a small amount of nanofiller. However, the same NM can modify differently the final NC properties depending on its dispersibility and interaction within the matrix. The objective of the present study is to analyze the different behaviour of PA6 NC filled with a 3% of compatibilized and non-compatibilized MWCNT or SiO_2 NP, to identify the modifications caused on the mechanical and structural properties, as well as to evaluate the possible aggregation, migration or release of the NM during the fabrication and use of the NC.

It is accepted that an homogeneous dispersion of the nanofillers within the matrix contributes in the improvement of the physical, chemical and mechanical properties of the NC. PA6 is essentially a hydrophilic polymer. Thus, beforehand, unmodified SiO_2 NP (with naturally formed –OH groups on its surface) and $MWCNT_{MB}$ (additived to obtain a high-loaded and homogeneous mixture of MWCNT) were expected to be more compatible with the matrix. Contrarily, hydrophobic SiO_2 NP, with octyl groups on NP surface, and pristine MWCNT, would be more likely to show worse compatibility with the hydrophilic polymeric matrix (PA6), and consequently resulting in NC with worse properties.

In order to study the different dispersion and structural properties provided by the NM and compare its modification between compatibilized and non-compatibilized samples, TEM and DSC analysis were performed. Ultrafine TEM sections of the inner part of each PA6 NC after injection showed a uniform distribution of the nanofiller in all the cases excepting for NC including hydrophobic SiO_2 NP, which formed aggregates due to their incompatibility with the matrix (figure 1). Contrarily to the hydrophilic SiO_2 NC, this aggregation resulted in an increase of the melting and crystallization enthalpies (table 2). Both MWCNT were homogeneously distributed within the matrix, though compatibilized $MWCNT_{MB}$ favours flame retardancy and PA6 crystallinity. Thus, a good compatibility NM-matrix guarantees the maintenance or improvement of the NC properties respecting the original polymer, which cannot be said for the non-compatibilized NM.

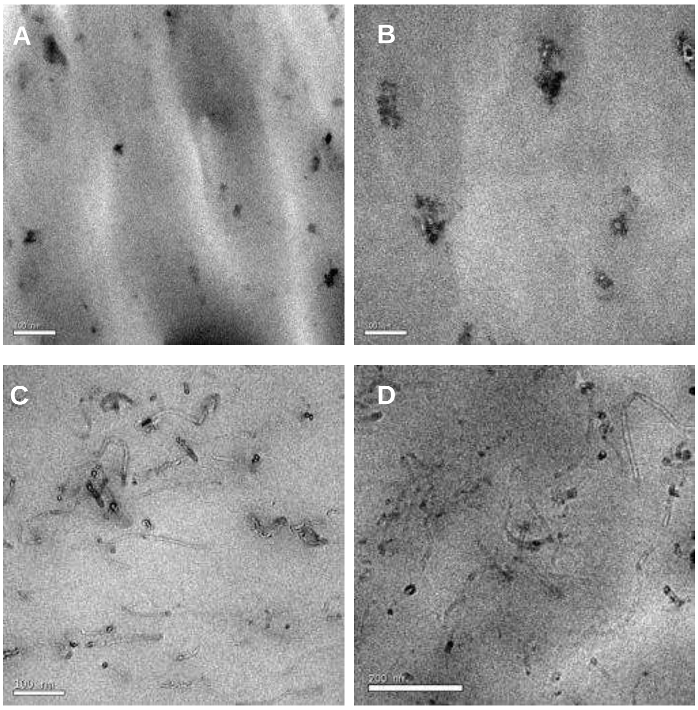


Figure 1. Section of specimen tests with a 3% of a) hydrophilic SiO_2, b) hydrophobic SiO_2, c) MWCNT and d) $MWCNT_{MB}$.

Table 2. Values of DSC and percentage of crystallinity

NC	midpoint T^a_c (°C)	ΔH_{cc} (J/g)	midpoint T^a_m (°C)	ΔH_{cm} (J/g)	crystallinity (%)
PA6	191,52	69,02	218,82	75,43	3,36 ± 0,02%
PA6 aged	191,02	79,14	214,51	87,95	2,86 ± 0,00%
PA6/SiO_2 hydrophobic	191,51	75,11	217,71	80,71	1,47 ± 0,57%
PA6/SiO_2 hydrophobic aged	191,565	74,86	217,04	78,83	1,04 ± 0,17%
PA6/SiO_2 hydrophilic	189,61	60,40	216,91	66,68	1,65 ± 0,01%
PA6/SiO_2 hydrophilic aged	190,94	69,47	216,06	73,64	1,09 ± 0,17%
PA6/MWCNT	196,09/209,62	57,95	220,04	60,47	0,66 ± 0,06%
PA6/MWCNT aged	244,765	71,38	261,08	84,99	3,57 ± 0,01%
PA6/$MWCNT_{MB}$	245,14	72,67	260,52	76,29	1,50 ± 0,13%
PA6/$MWCNT_{MB}$ aged	196,95/207,21	73,95	220,27	82,08	2,13 ± 0,08%

3.2. Influence of NM nature and compatibilization on NC aging

Apart from the production stage, the present work simulated usage of the NC by accelerated aging in controlled conditions to determine possible changes in this phase of their life cycle. The use of NC can change its physicochemical properties, cause its degradation, and affect the distribution or release of the nanofillers.

In order to determine the alteration of the NC due to aging, TGA, TEM and DSC analysis were performed. The TGA showed that the weight loss of organic mater (o.m.) is higher in all the aged NC excepting PA6/$MWCNT_{MB}$. It indicates the appearance of degradation products from the PA6 that are consumed at higher temperatures; the NC with compatibilized MWCNT is protected by the uniformly dispersed nanofiller, avoiding the mentioned degradation (table 3). It is also supported by TEM imaging, where PA6/$MWCNT_{MB}$ samples do not show detectable differences in NM dispersion and PA6 structure after aging, but it causes the fragmentation of all the other polymeric matrices (figures 2 & 3). In addition, regarding SiO_2 NC, TEM imaging shows that aging causes the aggregation of compatibilized and well-dispersed SiO_2 NP; this changes the properties of the NC, making them more similar to those observed in the non-compatibilized SiO_2 NC.

DSC characterization (table 2) shows that the different nature of SiO_2 NP and MWCNT affected differently the crystallinization of PA6. Compatibilized SiO_2 NP reduced the crystallinization temperature, though this effect was lost during the NC aging. Crystallinity, however, was reduced heavily in both compatibilized and non-compatibilized SiO_2 NC. Regarding MWCNT NC, the nanofiller had the opposite effect on PA6. Crystallinization started at higher temperatures, and this effect was much more evident when the nanotubes had been compatibilized. This is due to the nucleating effect that this nanomaterial causes in the process. When PA6-MWCNT had not been compatibilized, interactions between both components of the NC is worst, the nucleating effect is less notorious and occurs in two steps, which indicates two reordinations of the atoms. After aging, both MWCNT samples show an increase in the crystallinity values, specially the compatibilized sample.
Even both nanofillers have different effect on the polymer, it can be said that an increase of the compatibility between NM and matrix causes a decrease of the PA6 crystallinity. However, the nucleating effect of MWCNT leads to an earlier crystallinization.

Table 3. Thermal degradation (TGA) of polymer and NC

	non-aged		**aged**	
NC	**Weight loss 700ºC (o.m.)**	**i.m.%**	**Weight loss 700ºC (o.m.)**	**i.m.%**
PA6	99.14%	---	97.78%	---
PA6/SiO_2 hydrophobic	97.87%	1.21%	97.00%	0.81%
PA6/SiO_2 hydrophilic	97.49%	1.81%	96.75%	1.14%

NC	**Weight loss 600ºC (o.m.)**	**i.m.%**	**Weight loss 600ºC (o.m.)**	**i.m.%**
PA6	98.98%	---	97.02%	---
PA6/MWCNT	95.35%	3.70%	94.09%	1.97%
PA6/$MWCNT_{MB}$	94.16%	4.92%	95.70%	2.21%

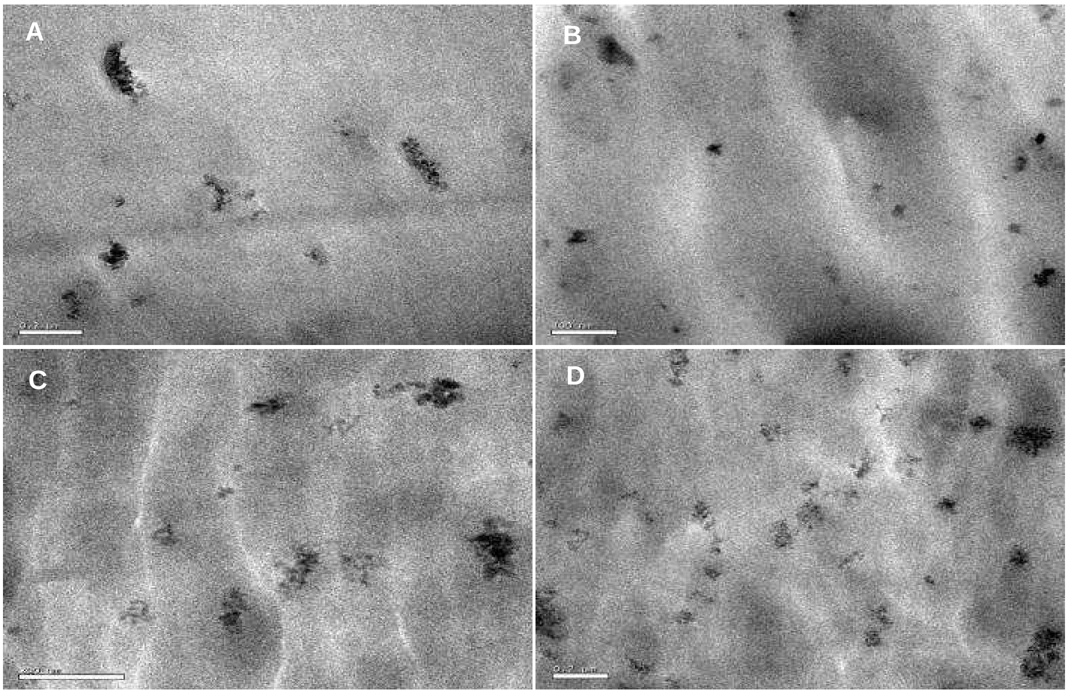


Figure 2. Image TEM of non compatibilized (A-C) compatibilized (B-D) non aged (A-B) and aged (C-D) SiO_2 NC.

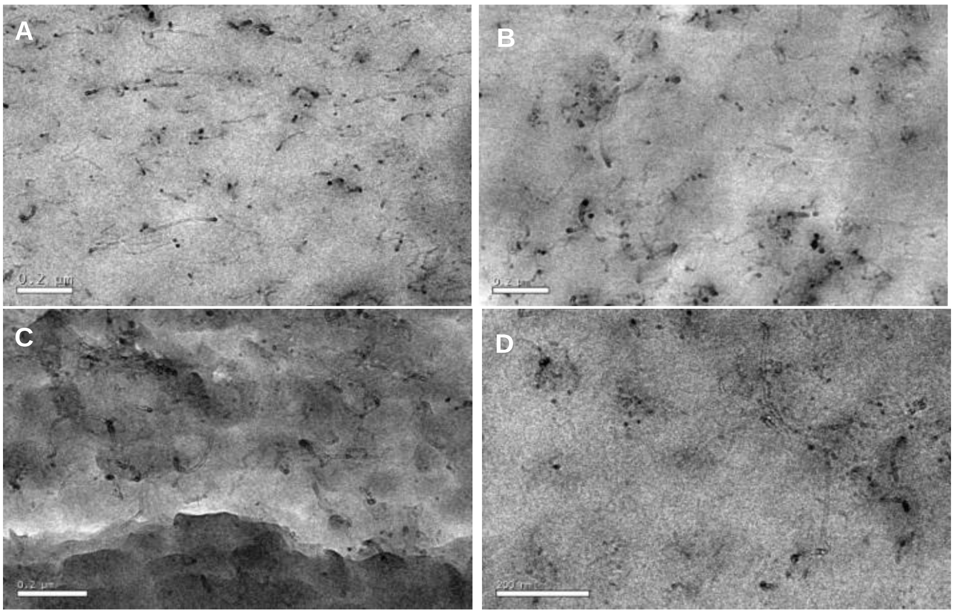


Figure 3. Image TEM of non compatibilized (A-C) compatibilized (B-D) non aged (A-B) and aged (C-D) MWCNT NC.

The degradation occurred in the NC during the simulation of its use (accelerated aging) is also observable in its surface by SEM-Merlin imaging. This technique allowed us to observe the external part of the NC without any extra treatment. After injection, SiO_2 NP and MWCNT were observable embedded in the matrix. However, after aging, both types of nanofillers were clearly on the surface, exposed to the environment (figure 4). Altogether with TGA data, which indicate a loss of i.m. during aging, results indicate that (being NM compatibilized or not) the degradation of PA6 causes the release of SiO_2 NP and MWCNT to the environment.

SEM images show same degradation degree of the matrix in its surface for both SiO_2 NC, as well as for non-compatibilized MWCNT NC. In these cases, it leads to the aggregation of the NM. It is important to mention that the aggregation of the non-compatibilized MWCNT was not observable in TEM, most probably due to a more accused degradation of PA6 in the surface. $MWCNT_{MB}$ samples seem to be more protected by the nanofiller, and there is no evidence of degradation or migration.

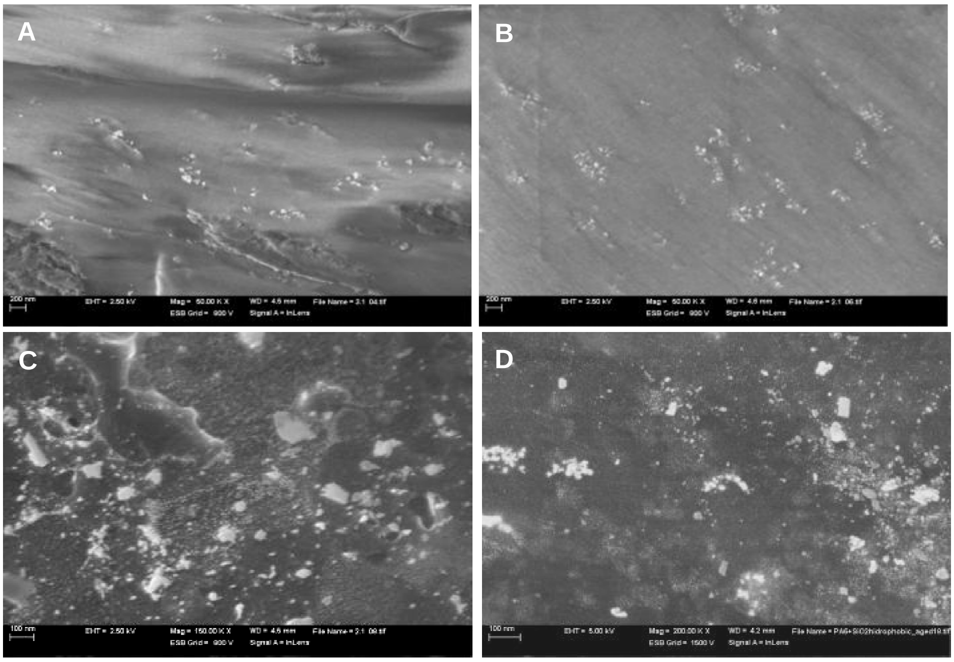


Figure 4. Image SEM of non compatibilized (A-C) compatibilized (B-D) non aged (A-B) and aged (C-D) SiO_2 NC.

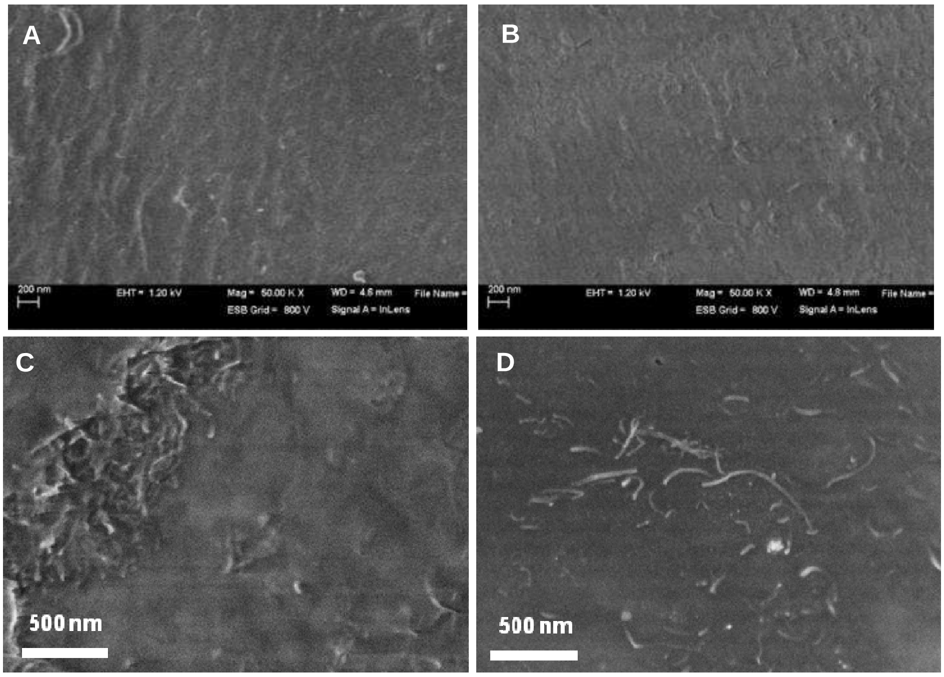


Figure 5. Image TEM of non compatibilized (A-C) compatibilized (B-D) non aged (A-B) and aged (C-D) MWCNT NC.

3.3 Extraction of the NM for recycling by calcination

In recent years, there has been an increasing interest in the use of NM to improve interesting properties of different polymers. Therefore, it is important to know what to do with these NM at the end of their life. There are different options; NC can be recycled (mechanical recycling) or it could be better recycling the NM or depending on their physicochemical properties and their toxicity the NM can be disposed. It is important to consider that the physicochemical properties could change during their useful life and therefore, their toxicity can also be affected. When this happen and in those cases that these new properties are not interesting, the NM have to be disposed.

In this project, calcination was chosen as a method to recover the NM from NC. A previous study about calcinations of raw NM was performed in order to determine the changes which could be due to the extraction process. Calcination conditions were 410°C during 3h 30 min. The temperature was determined according to the data obtained by TGA therefore, it was considered the temperature in which polymer is burned and NP do not suffer any change. Calcinated NM were characterized by FT-IR and TGA and neither of the two analyses showed any differences between NM before and after calcination except for the case of hydrophobic SiO_2 whose octyl groups are burned by calcination.

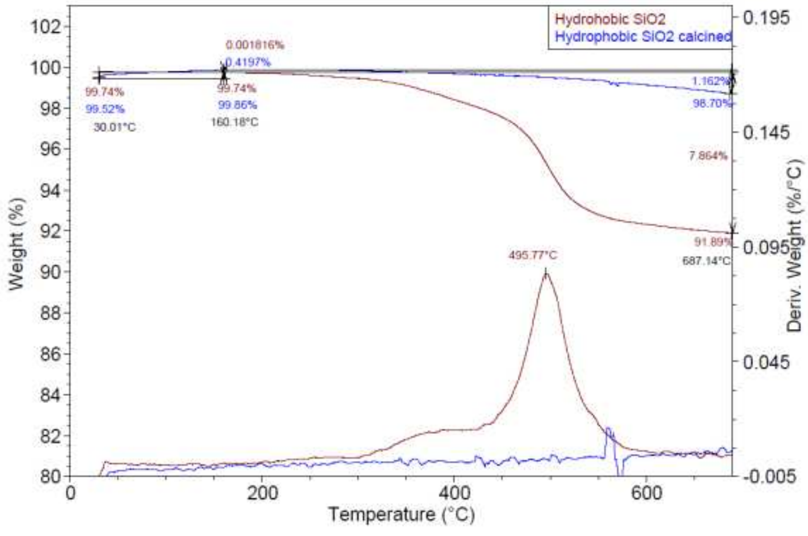


Figure 6. TGAs comparison between calcined and non calcined hydrophobic SiO_2.

Figure 6 shows a comparison between NM before and after calcination, and it can be observed that the loss of weight corresponding to the functional group of NM cannot be observed after calcination. Nevertheless, it was decided to calcinate all NC to recover NM because non functionalized SiO_2 NP can also be used in the synthesis of NC.

3.4. SiO_2 NP recovered

According to FT-IR analyses it cannot be observed any difference between NM recovered from compatibilized and non compatibilized NC. Recovered material exhibits bands which are associated to the vibrations corresponding to SiO_2 NP (1055 cm^{-1} and 806 cm^{-1} assigned at Si-O st and Si-O bd, respectively) and remaining polymer (1599 cm^{-1} and 3360 cm^{-1}).
Moreover, TGA results are consistent with those obtained by FT-IR. The first analyses showed a weight loss at ~600 °C which corresponds to remaining polymer. However, a curious behavior was detected in the case of hydrophobic SiO_2 NC. Figure 7 shows a comparison between hydrophobic SiO_2 NP non-calcinated and extracted material from aged and non aged SiO_2 NC. It can be observed that the weight loss at 496 °C, which is attributed at the octyl groups, cannot be observed in the case of extracted material from non aged SiO_2 NC indicating that these groups have been calcinated during processing but it is not so in the case of the material recovered from aged SiO_2 NC. This fact indicates that the degraded matrix is interacting with octyl groups in a way that protects these groups from degradation.

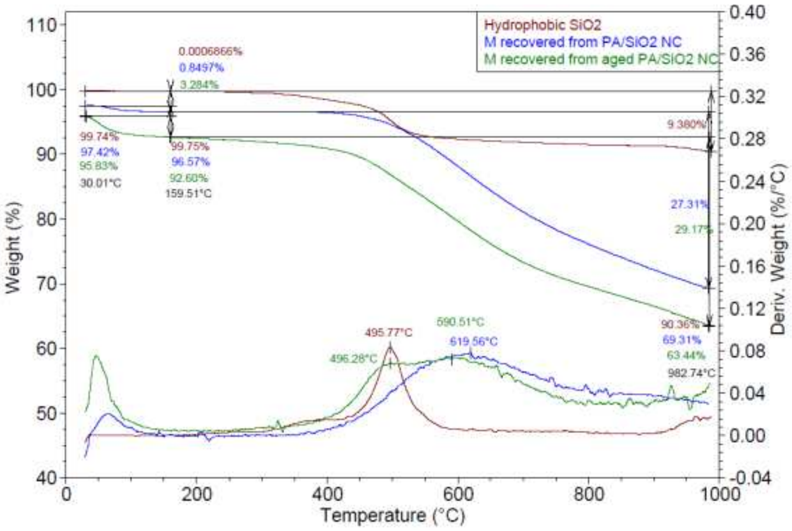
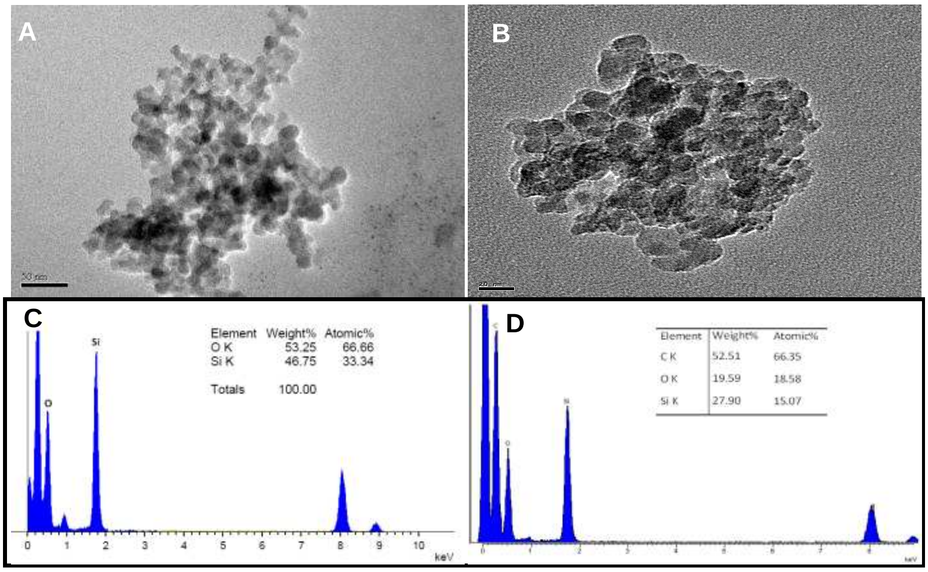


Figure 7. TGA comparison between hydrophobic SiO_2 and NM recovered from aged and non aged PA/SiO_2 NC.

The TEM images obtained from recovered material support these last results. NM recovered and some amount of polymer can be observed before and after aging processes, but in the last case, the amount of polymer remaining is higher. Their atomic composition was determined by EDX (figure 8).



Element	Weight%	Atomic%
O K	53.25	66.66
Si K	46.75	33.34
Totals	100.00	

Element	Weight%	Atomic%
C K	52.51	66.35
O K	19.59	18.58
Si K	27.90	15.07

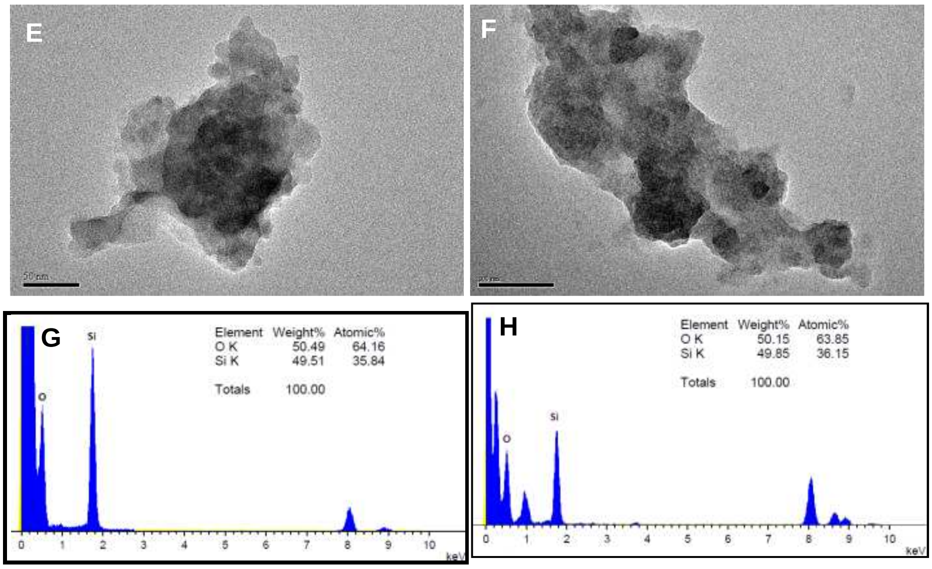


Figure 8. TEM images of material recovered from non-compatibilized (A-E) compatibilized (B-F) non-aged (A-B) and aged (E-F) NC. EDX spectrum of material recovered from non-compatibilized (C-G) compatibilized (D-H) non-aged (C-D) and aged (G-H) NC

3.5. MWCNT NM recovered

According with FT-IR and TGA, it is concluded that the material recovered from both NC contains MWCNT and polymer remaining. On the other hand, TEM analysis showed that the recovered material before the aging process consisted of MWCNT which are inserted inside the polymeric matrix and there are a little amount of them that are free. However, this tendency is different when the NC were aged. In these cases, it can be observed a big amount of MWCNT free and a small amount inserted in the polymeric matrix. Therefore, it can be concluded that the release of MWCNT from polymeric matrix is easier when the last has been affected by the aging process (figure 9).

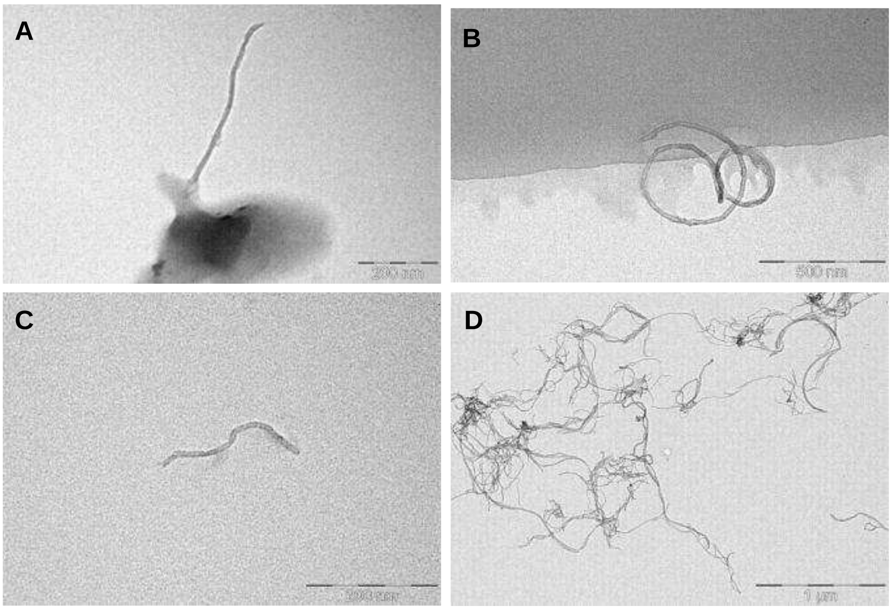


Figure 9. Image TEM of material recovered from non-compatibilized (A-C) compatibilized (B-D) non-aged (A, B) and aged (C, D) NC

4. Conclusions

Different PA6 NC were prepared using compatibilized and non compatibilized NM. The NM chosen were SiO_2 NP and MWCNT whose surface was modified in order to obtain different compatibilities between NM and polymer. Hence, hydrophobic SiO_2 NP (with octyl groups in their surface), hydrophilic SiO_2 NP, MWCNT in powder form and MWCN master batch were used.

Specimen NC were obtained by extrusion and injection processes and were aged by accelerated aging processes (outdoors simulation processes) in climatic chambers. Analysis of NC properties before and after ageing demonstrated that release of NM from polymer NC depends mainly on polymer degradation. The process of polymer degradation in NC materials under climatic conditions can be reduced by the inclusion of well-dispersed MWCNT. However in the case of SiO_2 NP degradation of the polymer is not dependent on the dispersibility of the nanofiller in the matrix. Therefore, the size, shape and chemical composition of the nanofiller was shown to influence the release of NM to the environment.

Calcination is the method proposed in this work to recover the nanofillers from NC for recycling. A preliminary study was performed to identify possible modifications in NM structure due to the method of the extraction; any modifications could be observed, to except of hydrophobic SiO_2 which lost their octyl groups. Therefore, NM can be recovered from NC with a small amount of polymer, and reused.

5. Acknowledgements

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