Exploring release and recovery of nanomaterials from commercial polymeric nanocomposites

To cite this article: Martí Busquets-Fité *et al* 2013 *J. Phys.: Conf. Ser.* **429** 012048

View the article online for updates and enhancements.

Related content

- Monitoring migration and transformation of nanomaterials in polymeric composites during accelerated aging
  G Vilar, E Fernández-Rosas, V Puntes et al.

- On Nanoparticles Release from Polymer Nanocomposites for Applications in Lightweight Automotive Components
  S Sachse, L Gendre, F Silva et al.

- The social context of nanotechnology and regulating its uncertainty: A nanotechnologist approach
  Vincent Jamier, Ignasi Gispert and Victor Puntes

Recent citations

- Assessment of Mass Transfer from Poly(ethylene) Nanocomposites Containing Noble-Metal Nanoparticles: A Systematic Study of Embedded Particle Stability
  Rebecca G. Weiner *et al*

- Non-linear release dynamics for a CeO $_2$ nanomaterial embedded in a protective wood stain, due to matrix photo-degradation
  Lorette Scifo *et al*

- Sensitivity Enhancement of Benzene Sensor Using Ethyl Cellulose-Coated Surface-Functionalized Carbon Nanotubes
  Thanattha Chobsilp *et al*

IOP ebooks™

Bringing you innovative digital publishing with leading voices to create your essential collection of books in STEM research.

Start exploring the collection - download the first chapter of every title for free.

Exploring release and recovery of nanomaterials from commercial polymeric nanocomposites

Martí Busquets-Fité[1,2,6], Elisabet Fernandez[3], Gemma Janer[3], Gemma Vilar[3], Socorro Vázquez-Campos[3], R Zanasca[4], C Citterio[4], L Mercante[4], Víctor Puntes[1,2,5,6,7]

[1]Catalan Institute of Nanotechnology (ICN), Campus UAB, 08193 Bellaterra, Spain
[2]Universitat Autònoma de Barcelona (UAB), Campus UAB, 08193 Bellaterra, Spain
[3]LEITAT Technological Center. C/ Innovació 2, 08225 Terrassa, Barcelona, Spain
[4]LATI Industria Termoplastici S.p.A. , Vedano Olona, Italy
[5]Institució Catalana de Recerca i Estudis Avançats (ICREA), Passeig Lluís Companys, 23, 08010 Barcelona, Spain
[6]Centre d'Investigacions en Nanociència i Nanotecnologia CIN2 (ICN-CSIC), Campus UAB, 08193 Bellaterra, Spain.
[7]Author to whom any correspondance should be addressed

E-mail: victor.puntes@icn.cat

Abstract. Much concern has been raised about the risks associated with the broad use of polymers containing nanomaterials. Much is known about degradation and aging of polymers and nanomaterials independently, but very few studies have been done in order to understand degradation of polymeric nanocomposites containing nanomaterials and the fate of these nanomaterials, which may occur in suffering many processes such as migration, release and physicochemical modifications. Throughout the UE funded FP7 project NANOPOLYTOX, studies on the migration, release and alteration of mechanical properties of commercial nanocomposites due to ageing and weathering have been performed along with studies on the feasibility of recovery and recycling of the nanomaterials. The project includes the use as model nanocomposites of Polyamide-6 (PA), Polypropylene (PP) and Ethyl Vinyl Acetate (EVA) as polymeric matrix filled with a 3% in mass of a set of selected broadly used nanomaterials; from inorganic metal oxides nanoparticles (SiO2, TiO2 and ZnO) to multi-walled carbon nanotubes (MWCNT) and Nanoclays. These model nanocomposites were then treated under accelerated ageing conditions in climatic chamber. To determine the degree of degradation of the whole nanocomposite and possible processes of migration, release and modification of the nanofillers, nanocomposites were characterized by different techniques. Additionally, recovery of the nanomaterials from the polymeric matrix was addressed, being successfully achieved for PA and PP based nanocomposites. In the case of PA, dissolution of the polymeric matrix using formic acid and further centrifugation steps was the chosen approach, while for PP based nanocomposites calcination was performed.

1. Introduction The first section in your paper

Continuous increase on production of nanoparticles and other nanomaterials during last decades [1] has yield to extensive studies and characterization of their properties at the many stages of their life cycle [2-6]. The same happened for the most broadly produced commercial polymers. Nevertheless, when both are combined forming nanocomposites most of the studies and characterization effort has been focused on the emerging and enhanced mechanical properties of these new nanocomposites [7-

13], and little attention has been drawn to the evolution and processes suffered by the nanomaterials used as fillers [14-15]. This is because the nanofillers have been often considered to be trapped and stabilized into the polymeric matrix, and so the consequences of its interaction with the outside environment almost neglected. This inactivity of the nanomaterials used as nanofillers could not be so categorical and there could be release of material containing nanofillers (microsized or nanosized pieces of composites or even isolated or aggregated nanomaterial). Consequently, if there is release of material, potential exposure of nanomaterial has to be addressed and (combined with toxicological and (eco)toxicological data) risk for human health and environment must be determined.

In addition, if nanocomposites are going to be (and already are in some specific fields such as in automotive industry) produced at large scales, it is also crucial to study how to deal with them when they get to the end of their life in terms of both recycling and disposal.

All these aspects concerning nanocomposites, amongst other aspects of their life cycle, such as studies of potential migration and agglomeration/aggregation processes of the nanofillers due to aging, recycling of the nanocomposites by mechanical processes, extraction and reuse of the nanofillers, toxicological and ecotoxicological studies, life cycle assessment (LCA) studies and others are addressed by the project NANOPOLYTOX (funded by the European Community's Seventh Framework Program FP7/2007-2013).

NANOPOLYTOX is a preeminently industrial orientated project where 18 nanocomposites were generated by the combination of three of the more commercially produced polymers: Polyamide-6 (PA), Polypropylene (PP) and Ethyl Vinyl Acetate (EVA) with a 3% in mass charge of 6 largely produced nanomaterials: 3 metal oxide nanoparticles (SiO_2, TiO_2 and ZnO); multi-walled carbon nanotubes (MWCNT) and and two variations of organomodified montmorillonite (MMT) nanoclays (the quaternary ammonium modifiers dimethyl dihydrogenated tallow ammonium (CECA, France) and dimethyl benzylhydrogenated tallow ammonium (Stepan, USA)). It is important to note that in order to achieved good compatibility between the nanomaterials and the polymeric host, a prior tailored functionalization of the nanomaterials surface was performed. As an example, to make metal oxide nanoparticles (MOx) surface compatible with the highly hydrophobic polarity of polypropylene (PP), they were conjugated with either octyl or propyl capped groups.
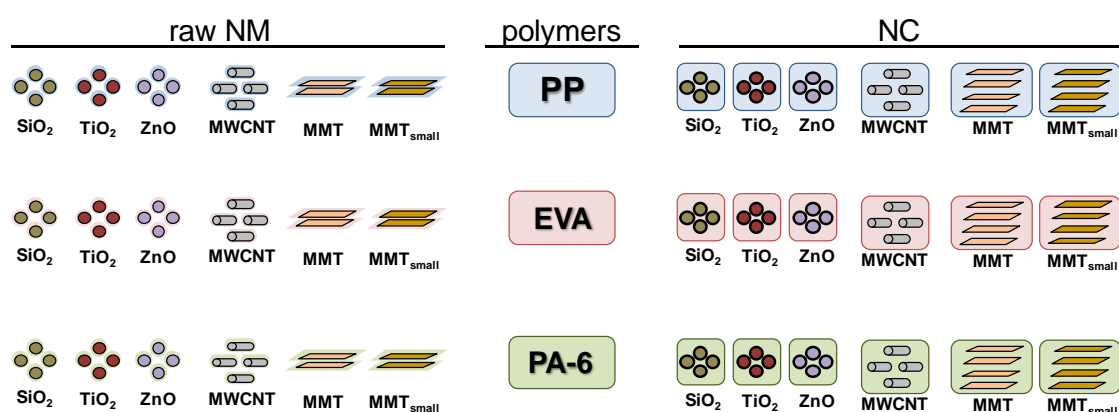

Figure1. General Scheme of the composites produced and studied within NANOPOLYTOX project (left column, under Nanocompoistes (NC) label) prepared combining three broadly produced polymers (central column; PP,EVA and PA-6) and broadly used used nanomaterials (labeled as raw NM)

An accelerated aging and weathering process was then applied to each nanocomposite inside aging chambers to study the evolution of both the whole composite and the nanofillers throughout the aging

process and possible release of material. As mentioned, a substantial part of the project deals also with the development of recycling, recovery and disposal processes.

In this article we present our results on the release due accelerated aging processes and on the extaction and recovery of nanomaterials from both PA and PP based nanocomposites are presented. Analysis on the data on the composites containing nanoclays is still not finalized so it will be presented in future work.

2. Experimental procedures

2.1 Conditions of the accelerated aging process
Each nanocomposite underwent an accelerated aging and weathering process equivalent to 10 years of normal aging following the normative *UNE-EN ISO 4892-2/06, and* consisting of 1000 hours of weathering cycles under UV light and simulated heavy rain episodes. The thecnical details are as follows:

Continuos UV irradiation (340nm): 0,50 W/m^2

Black Strandard Temperature (BST) conditions: 65 ± 3ºC

Relative Humidity: 50 ± 5%

Wetting cycle: 1± 0,5 min

Drying: 29 mins

Filters: Borosilicate

2.2 Procedures of extraction and recovery of nanofillers

2.2.1 Extraction and recovery of nanomaterials from Polyamide-6 based composites In order to recover the nanomaterials incorporated to the PA polymeric matrix, the chosen approximation was the dissolution of the mentioned polymer using concentrated formic acid (HCOOH). The method was optimized to maximize the amount of polymer that can be dissolved at once. It consisted on the dissolution of PA-based composite pieces in formic acid 95%, and the recovery of the nanomaterials after several series of washing and centrifuging processes with fresh formic acid 95% and ultrapure water. A final drying step under vacuum was needed to obtain the recovered nanomaterial as dry powder. The optimized lab-scale extraction and recovery method is as follows:

- **Dissolution Step:** Cut the composites into small pieces (0.5g-2g) and dissolve between 7g and 9g of the composite into 40mL of formic acid, using 50mL centrifuge tubes (made of PP). Complete dissolution takes between 2 and 4 days depending on the quantity of composite and the regularity of the shaking of the tubes. Three shaking operations, consisting of few seconds shaking and an upside down turn of the tubes, per day are enough for a complete dissolutions in 48h.

- **Centrifugation and washing steps:** Once the composite is fully dissolved, centrifuge the sample (the longest and under more times gravity force, xg or g's). Decant the dissolved polymer. Washed and centrifuged the obtained solid twice with 10mL of fresh formic acid and then again twice with 10mL of ultrapure water. The reason of using fresh formic acid for the first two washings is to get

rid of polyamide residues, because if the pH of the media increases while there is still a relevant concentration of polyamide it automatically precipitates again into solid polyamide, compromising the purity of our recovered material. As was said before, each kind of nanocomposite requires different centrifugation times and speeds. The optimal numbers are shown in the table below in **Table1.**

- **Drying Step:** Dry out carefully the recovered and washed material under vacuum conditions.

Table 1. Optimal centrifugation conditions for each type of nanomaterial. G's stands for times gravity force

Type of NM	1st Centrifugation (dissolved polymer)		Formic acid washings+ centrifugation 2 x 10mls		mQ washings + centrifugation 2 x 10mls	
	mins	g's	mins	g's	mins	g's
Metal oxides	15	7000	5	6000	5	6000
Clays	20	10000	5	9000	5	9000
MWCNTs	40	13000	10	11000	10	11000

2.2.2 Extraction and recovery of nanomaterials from Polypropylene based composites The mildest methods attempted to dissolve PP were too aggressive for nanoparticles and implied an important affectation of its functionalization and inorganic structure. For that reason, dissolution approach was dismissed and replaced for calcination approach. Conditions used were 430°C for 3h and 30min, selected to both achieve a virtually complete degradation of PP into CO_2 and allow further characterization of the recovered material using thermogravimetry (TGA).

3. Results and discussion Another section of your paper

3.1 Studies on the release during accelerated aging process

To study the release of material due to the accelerated aging and weathering process, the aging waters were collected and lyophilized. The values of released mass, without determining yet its nanometric or micrometric nature or composition, can be seen in Figure2 in % of mass released found on the aging waters respect the initial mass of composite. The values themselves give no information as the percentage of mass released may vary depending on the duration of the aging process and the shape (or exposed surface) of the sample, but they are valuable to compare between composites and extract some information. EVA based nanocomposites show much less loss due to aging than PA or PP, One may think that is because of a higher resistance to degradation, but a closer evaluation of the TEM and SEM imaging data of the microtomo cuts of the nanocomposites before and after undergoing the aging process reveals that the ones with higher release values were the ones with more clearly observable aggregates and segregates of nanomaterial, of even few microns in the worst cases (PA6-ZnO-OH one). This is most probably due to a not totally efficient conjugation of the surface process, and thus, a decrease of compatibility between nanofillers and polymeric matrix. In the case of EVA composites we can attribute the lower release values to the fact that the metal oxide nanoparticles no dot require an extra conjugation step to make their surface compatible with the polarity of the polymeric matrix host, because they already are compatible.
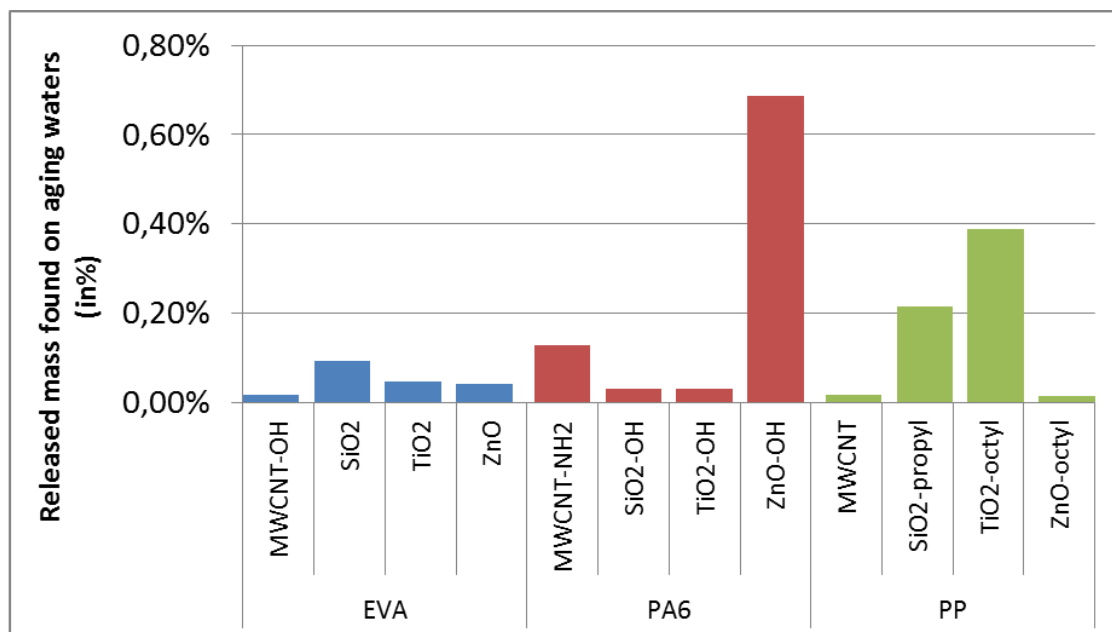
Figure2. Graphic in bars showing the percentage of released material collected in the aging waters during the accelerated aging and weathering process. In % respect the initial total mass of composite.

Characterization of the material found in the aging water was limited by the amount of material recovered, as some techniques require higher amounts than the actually found material. Nevertheless, TEM imaging using EDX to identify the composition (even quantitatively) gave 2 different kinds of behaviors in terms of nanomaterial content on the material found on the lyophilized aging waters. The extreme cases were the PP-SiO2-Propyl and PP-MWCNT composites were in the first case many SiO2 nanoparticles were found by TEM and confirmed by EDX to be the 19,9% in mass of the total material (7 times higher content than the original 3% charge of all composites) while no hints of MWCNT were found and only few pieces of polymer were observed (see Fig.Y). This observations match with both release due to degradation and goodness of the mixing observed by TEM and SEM of the composites microTomo cuts, in the sense that when the compatibility is not well achieved, there was obseeved more release of material during aging and there is more presence of nanomaterial in to the released material.
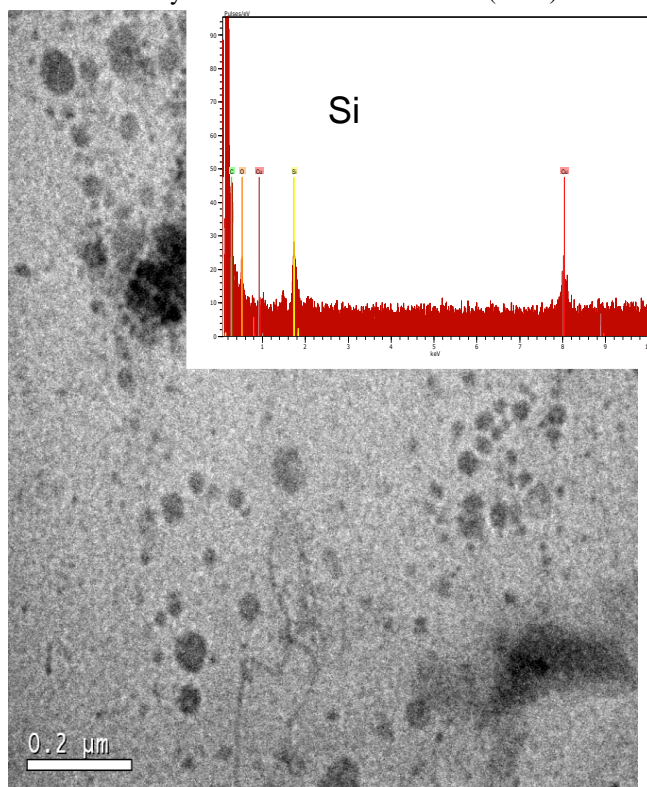
Figure3. Background: TEM image of material recovered from PP-SiO2-Propyl nanocomposite.**Inset:** EDX spectra of the recovered material from PP-SiO2-Propyl nanocomposites, where quantification showed a 19.9% in mass presence of SiO2 on the released material

Further analysis and collection of bigger amounts of aging waters will be done to corroborate the results presented here. If confirmed, it would be possible to categorize the samples into composites releasing nanomaterials and composites not releasing them. Then exposure matters, and further (eco)toxicological assays would only have to be addressed for the ones where release and exposures is actually taking place.

3.2 Discussion on the extraction and recovery of nanomaterials
3.2.1 Discussion on the extraction and recovery of nanomaterials from Polyamide-6 based composites
After the whole dissolution plus centrifugation and washing process, powder-like material was recovered in yields between 43% and 60% respecting to the original 3% charge of the nanomaterial (see **Fig4.**). Characterization of the recovered materials showed a huge change in some surface properties such as BET surface area, which combined with TGA spectra and TEM imaging indicates an incomplete removal of PA residues. Nevertheless, ICP-MS values of the metalic elements (Ti in case of TiO_2 and so on) are not in any case statistically significantly lower.
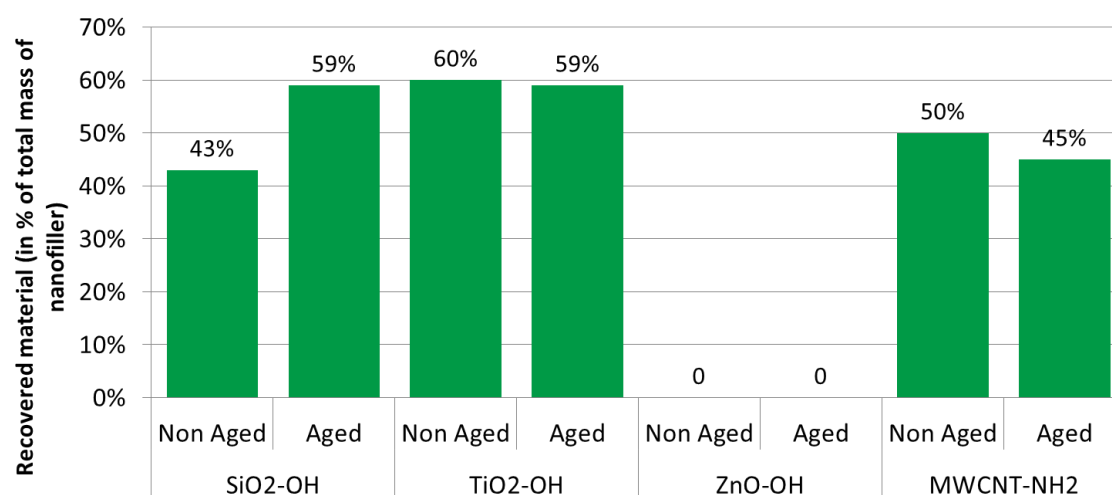

Figure4. Yields of recovery of extracted and recovered materials from PA based nanocomposites

In the case of the composites containing ZnO, the developed dissolution with formic acid method is not valid due to the high acidity of the media and the well-known high reactivity towards ionization (Zn^{2+}) of ZnO nanoparticles. Then is not possible to recover them in nanoparticulate solid form.

Another remarkable consequence of this dissolution approach to extract and recover nanoparticles is that, even with the aggressiveness of the procedure, the surface conjugation is kept almost unaltered. This is clearly seen by FTIR spectroscopy, where all the peaks corresponding to the functional groups (−OH and Si-O-C vibration bands) are still present (**see Fig.5-B**)
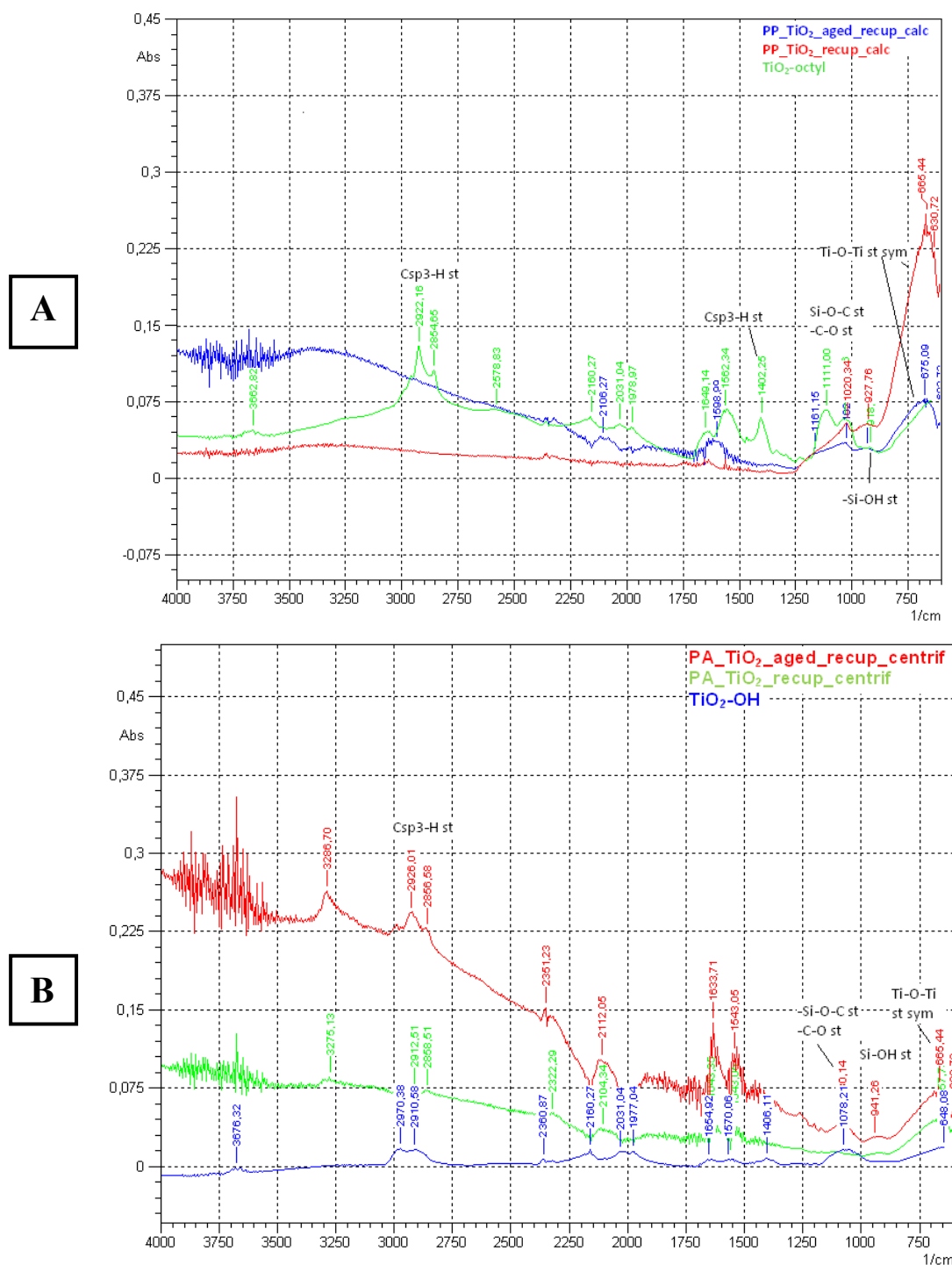
Figure.5 A) The figure shows a comparison among FTIR spectrum of extracted material from PP+TiO$_2$ aged and non aged nanocomposites and TiO$_2$-octyl. The FTIR analysis indicates the presence of TiO$_2$ NP characteristic bands (Ti-O-Ti symmetric stretching at 680 cm^{-1}), whilst the bands corresponding to the functional group (C$_{sp}^3$-H stretching at 2922 and 2855 cm^{-1}, C$_{sp}^3$-H bending at 1402 cm$^{-1)}$ cannot be observed, indicating its loss. Even so, the band corresponding to silica (-Si-OH and Si-O-C stretching mode at 928 cm^{-1} and 1020 cm^{-1} respectively) used to attach the octyl group to TiO$_2$ nanoparticles can be observed indicating that it is not eliminated during the calcination process. **B)** Comparison between the FTIR spectra of starting nanomaterial TiO$_2$-OH and the extracted materials from PA (non-aged/aged nanocomposites). The FTIR analysis indicates the presence of the TiO$_2$ NP characteristic band (Ti-O-Ti symmetric stretching at 665 cm^{-1}) in all the samples. Additionally, the bands corresponding to the silica (-Si-OH and Si-O-C stretching modes at 928 cm^{-1} and 1020 cm^{-1} respectively) used to attach the –OH group to the TiO$_2$ nanoparticles surface, and the bands corresponding to the functional group (C$_{sp}^3$-H stretching at 2922 and 2855 cm^{-1}, C$_{sp}^3$-H bending at 1402 cm^{-1}) can be seen as well. This fact implies that the functional groups were not eliminated by the extraction process.

Maintaining the surface conjugation and at the same time a small residual polyamide could turn out to be a huge advantage by the time to recycle the recovered material to produce new PA based nanocomposites as it could be avoided an extra conjugation step to add functional groups into the surface and the material could be treated as a master batch for the production of new PA composites.
During the dissolution process significant amounts of dissolved PA in highly acidic formic acid was produced. However, far from being treated as waste, it can be used to recover and reuse again the PA. Actually, it is a very commonly used industrial way to recycle PA from old polymers.

3.2.2 Discussion on the extraction and recovery of nanomaterials from Polypropylene based composites Very high yields of recovered material from calcinations of nanocomposites were obtained (see Fig.6) of above 95% for all of them but for the PP-MWCNT aged one. Yields were corrected taking into account that calcinations of PP alone gave a total residue of 0.41% of the initial composite mass.
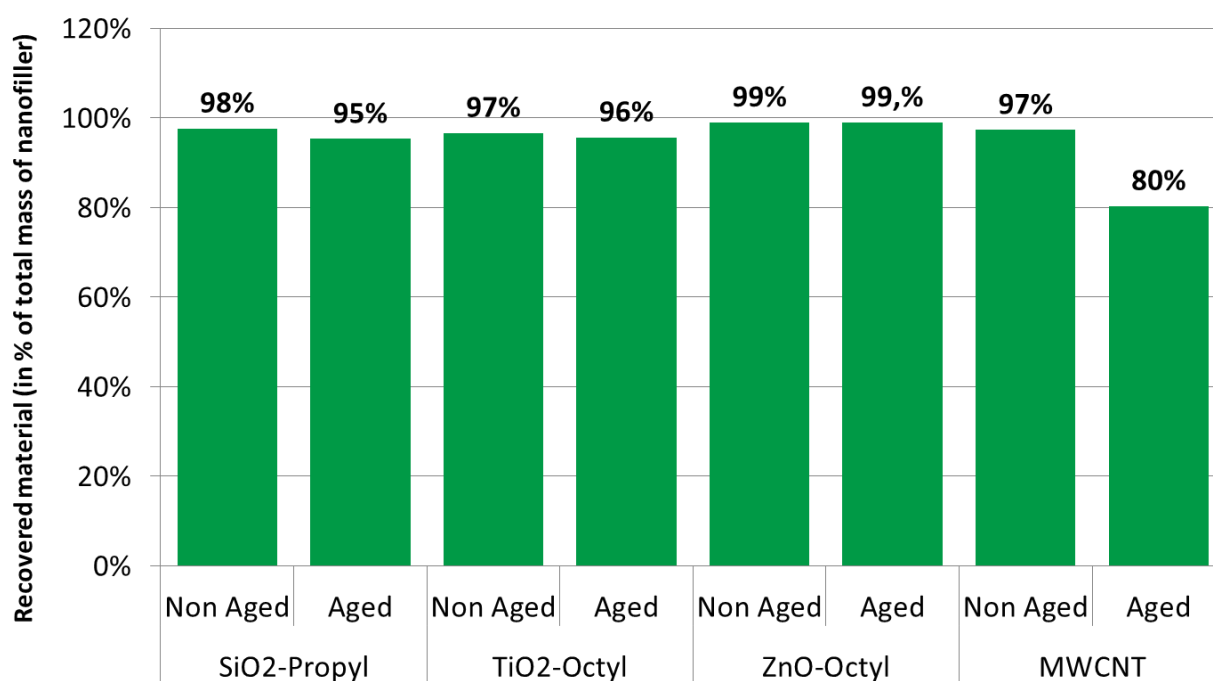

Figure 6. Yields of recovery of extracted and recovered materials from PP based nanocomposites

It is remarkable that even under such thermal conditions (430ªC) for 3h 30min, no sintering phenomena was observed by TEM imaging. This may be due to the low charge of nanofillers (3%) and the presence of the PP polymeric matrix, that keeps the particles mostly isolated and separated one from each other while degrading, preventing them from being in contact and, thus, from suffer sintering.

Regarding the conjugation of the surface, in contrast with the material extracted and recovered from PA composites following a dissolution approach, there is an almost complete lost of the surface modifiers during the calcination process, observable in Fig5-B, where the peaks corresponding to the -octyl modifier are almost not present in both spectra of aged and non-aged calcinated PP+TiO$_2$-octyl nanocomposites. This may then be a drawback if we intend to reuse these recovered nanomaterials to be extruded again into a PP based nanocomposites, as for that purpose an extra conjugation step would be mandatory.

4. Conclusions

Regarding release of material due to accelerated aging: Release of material has been found for all the tested composites, but exposure, and so potential risk, only would have to be addressed for the ones were nanomaterial rather than only polymer has been found. Then it turns out that a good functionalization of nanomaterials surface to make them compatible with the polarity of the polymeric host is a key factor to determine the degree of degration upon aging of the resulting composite Further (eco)toxicity results will determine their hazard and risk, but released material is low, under 0.7% of mass in the worst case and less than 0.05% of the orginal mass in the majority of the testes nanocomposites

Regarding extraction and recovery methods: Calcination of PP nanocomposites gave higher yields of recovery ($\approx$100%) than PA dissolution (40-60%), though the morphology and distribution of the organic core remains almost the same in both cases. PA preserves the organic surface modifier, which confers compatibility between the nanofillers and the polymeric host, and keeps a certain amount of PA residue, which combined make the recovered material a perfectly suitable master batch to be recycled again into a new nanocomposite. On the other side, calcination of PP yields to nanomaterials with an almost complete loss of the functional groups, and would need to undergo an extra surface conjugation step in order to be used again to produce new PP nanocomposites.

References
[1] Hendren C O, Mesnard X, Dröge J and Wiesner M R 2011 *Environmental Science & Technology* 2011 **7** 2562-2569
[2] Adams L K, Lyon D Y; Alvarez P J 2006 **40** 3527– 3532
[3] Klaine S *J Environ. Toxicol. Chem.* 2008 **27** 1825– 51
[4] Nel A 2006 *Science* **311** 622– 627
[5] Davis J M 2007 *J. Nanosci. Nanotechnol.***7** 402– 409
[6] Wiesner M R 2006 *Environ. Sci. Technol.* **40** 4336– 4345
[7] Usuki A, Kawasumi M, Kojima Y, Okada A, Kurauchi T and Kamigaito Osami 1993 *Journal of Materials Research* **8** 1174.
[8] Usuki A, Kojima Y, Kawasumi M, Okada A, Fukushima Y, Kurauchi T and Kamigaito Osami 1993 *Journal of Materials Research* **8** 1179.
[9] Bhattacharyya, A R, Sreekumar T V, Liu T, Kumar S, Ericson L M, Hauge R H and Smalley R E 2003 *Polymer* **8** 2373-2377
[10] Assouline E., Lustiger A., Barber A H., Cooper C A., Klein E, Wachtel E. and Wagner H D 2003 *J. Polym. Sci., Part B: Polym. Phys.* **5** 520–527.
[11] Kearns J C and Shambaugh R L 2002 Journal *of Applied Polymer Science* **8** 2079–2084.
[12] Moore E M, Ortiz D L, Marla V T, Shambaugh R L and Grady B P 2004 *Journal of Applied Polymer Science* **6** 2926–2933.
[13] Masenelli-Varlot K, Reynaud E et al. 2002 Journal *of Polymer Science Part B: Polymer Physics* **3** 272-283.
[14] Wohlleben W, Brill S et al. 2011 Small **7** 2384-2395.
[15] Reijnders L 2009 **94** 873-876.