Final publishable report

FP6 Project: NMP3-CT-2005-516972

NANOHYBRID

Designed Nanostructured Hybrid Polymers: Polymerisation Catalysis and Tecton Assembly

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Instrument: STREP
Thematic Priority: Priority 3 NMP
Project starting date: 01/03/2005
Project duration: 36 Months

Coordinator: ISMAC (I)

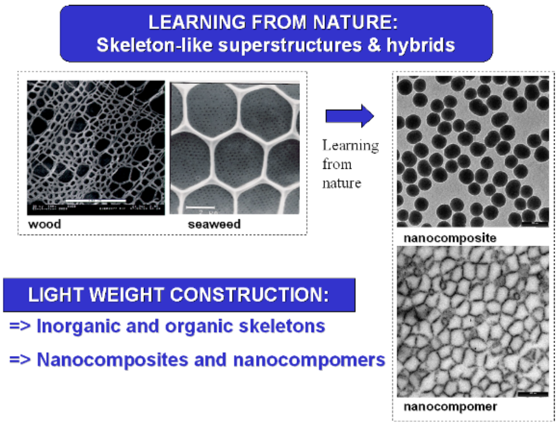
Partners: ICCOM (I)
CDCMP (I)
UMH (B)
FMF (D)
RWTH (D)
CEA (F)
STUBA (SK)
SASOL (D)
BASELL (I)
CEBAL (F)
CRF (I)
NANOCYL (B)
ALMA (F)
APBS (F)

Period covered: 01/03/2007 to 29/02/2008
Date of report: 09/05/2008

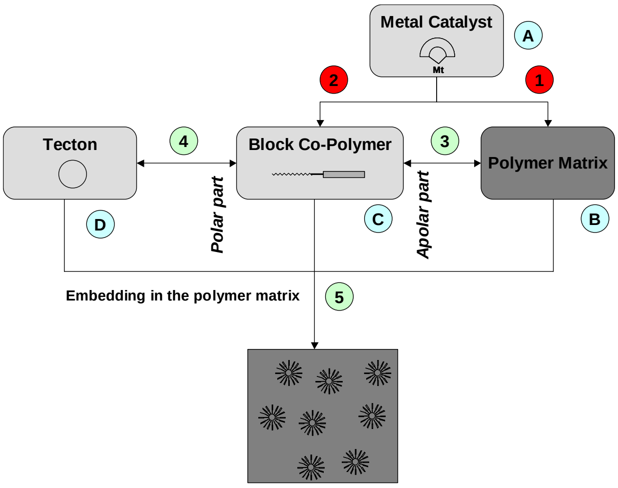
Project objectives

Learning from nature, the major objective of the Nanohybrid project is to develop fundamental knowledge in order to be able to elaborate new melt processable nanophase-separated hybrid materials with controlled architecture, derived from low cost petrochemical olefin feedstocks without sacrificing easy polymer melt processing.

To achieve the global objective leading to the design of **melt processable nanophase separated polyolefin hybrid materials usable in various industrial applications** the project focuses on:



- Creation of new knowledge related to **macromolecular architecture designs via transition metal catalysis** which will open up access to **novel random** and **block copolymers (BCs)** and polymer product compositions.
- Understanding the phenomena of **nanocompomers'** and **nanocomposites' formation** either **during in-situ polymerisation or** during **melt processing**
- Investigation of fundamental **characteristics** of the **organic-inorganic interphase** region by **multi-scale analysis**.



- **Various applications** are **targeted** in the **long term**. Early exploration will take place in the project in order to assess the capabilities of the NANOHYBRID material, and in view of further adaptation to these industrial processes.

The current polyolefin-based nanocomposites encounter difficulties with dispersion of tectons in the matrix (polyolefins are non-polar).
On the contrary to most current nanocomposites, where mainly physical bonding between nanofiller and matrix are obtained, the NANOHYBRID project will strive for combining chemical and physical bonding which would allow a real breakthrough in material's properties.
The tecton will be dispersed as nanofillers during melt processing or dispersed and assembled in the polymer matrix (in case of in-situ formation).

The synthesis and exploration of novel transition metal and rare earth metal catalyst systems for the efficient and controlled polymerization of various olefins is a main focus. Novel metal catalysts will play a key role in the strategy of synthesis of block copolymers as well as in the supporting on tectons. Moreover, polar and apolar diblock (AB) copolymers will give *stable organic inorganic interphase for novel hybrid polyolefins*.
Single site catalysts supported on tectons for in situ (filling) polymerisation will *produce nanoparticles coated with polymer as easy-to-disperse intermediates for novel nanohybrids with high inorganic content*.

Furthermore, the production of nanometer-scaled tectons, is expected to open up new ways to better performing polymer composites.
A better understanding and control of the catalysts, tectons and resulting nanohybrids will eventually enable the production of advanced nano-structured polymers with superior properties for new applications and products.

Work performed

Catalysts: Novel transition metal and rare earth metal catalyst systems have been synthesized: i) a number of monocyclopentadienyl Ln compounds (Ln = Sc, Y, Lu) for the controlled polymerization of olefinic and polar monomers: ii) cobalt and iron based (imino)pyridyl systems for the contemporaneous oligomerization/polymerization of ethylene. The rare earth complexes were tested for styrene, olefin, and ethylene-norbornene copolymerization. A method for tandem polymerization has been set up by combining the Co^{II} and Fe^{II} complexes with metallocenes and a suitable cocatalyst.

Novel polymers and block copolymers: The conditions under which newly developed bisphenolato metal complexes allow living styrene polymerizations have been investigated. Kinetics experiments to demonstrate the living ethylene-norbornene copolymerization with scandium dialkyl catalysts have been performed. Investigations on random copolymerization of norbornene bearing polar groups ($-CH_2OH$) as well as experiments to synthesize di-block copolymers having one block based on ethylene-norbornene copolymers and one block containing functionalized norbornene have been carried out.
Polymerization of ethylene and ethylene together with hexene have been performed in presence of diethyl zinc as chain transfer agent to obtain oligomers suitable for functionalization, which could be used as compatibilizers or as intermediates to obtain block copolymers.

Tectons and nanostructured hybrid polyolefins: Different doped and non-doped aluminas, silica-aluminas, and hydrotalcites aluminas to cover a wide range of surface acidities were developed. Organic acids were used to modify the alumina. Methods for the production of multiwall carbon nanotubes and for the controlled functionalization of carbon nanotubes have been designed and tested.
Catalytic in situ olefin polymerization and copolymerization on boehmites and on carbon nanotubes have been performed in order to compare the properties of nanocomposites obtained in situ with those prepared by melt blending. Multi-wall carbon nanotubes (MWNT) and DISPERAL were melt-compounded with high density polyethylene (HDPE) and isotactic polypropylene (i-PP), respectively by varying the filler content. Model nanocomposite of PP-CNT and of PP-DISPERAL fibers were prepared.

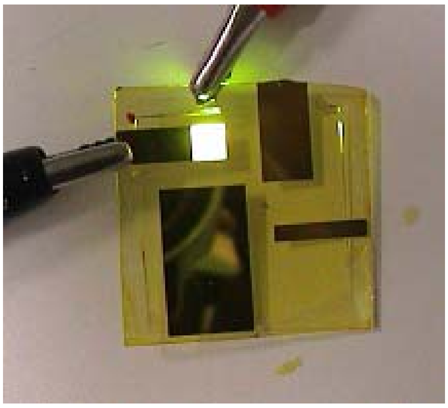
The multiscale analysis of the nanocomposites prepared *in situ* and by melt blending has been performed:

- at nano and micro scales to study the morphology and structure development at nano and micro scale (nano: AFM, Synchrotron, micro: TEM, EDX, XRD, XPS, SIMS, SEM, UV, vis, NIR spectroscopy, and DMA).
- at macro scale (rheology, mechanical properties, thermal degradation, flame retardancy, thermal analysis using DSC and TGA).
- the molecular modeling of polymer structures and properties.

The thermal stability, barrier, electrical and fire-retardant properties of the obtained nanocomposites containing MWCNTs have been investigated. Similarly, melt compounding masterbatches of PE/DISPERAL hybrid materials resulted in improved mechanical properties. Morevover, electro-optical properties of polymer CNTs hybrid composites for the

application in MOEMS (Mechanical Optical Electrical Micro System) devices have been studied.
The optimal composition and preparation (spinning and drawing) conditions from the point of tenacity and modulus of PP-CNTs and DISPERAL based composite fibres were defined.
The ageing of nanocomposites with alumina and carbon nanotubes has been investigated by studying their thermo-oxidation leading to the understanding of mechanism of degradation (at the same time, materials are aged by thermal and UV oxidation) and to the proposal of a stabilization system.

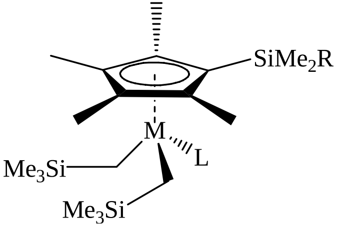
Among the possible *applications* those selected on which tests have been carried out *are:* an *automotive component (interior trim*) made of polypropylene (PP) by injection moulding process; elastomeric materials for *the support of fuel cell*; the fabrication of the *MOEMS* device and of a micro channelled cooler system for MEMS, *model textile fibres* based on *PP/MWCNT* and *PP/Disperal* 40 composites.



Proof-of-concept OLED device (CRF)

Results achieved, intentions for use and impact

Series of rare-earth metal bisalkyl half-sandwich complexes [Ln($C_5Me_4SiMe_2R$)(CH_2SiMe_3)$_2$L] (Ln = Sc, Y, Lu; R = Me, Ph, C_6F_5, 2-pyridyl, 2-furyl, 2-(5-Me)-furyl; L = THF) has been developed and tested successfully for styrene and olefin (co)-polymerization, ethylene/styrene (co)-polymerization, and ethylene-norbornene copolymerization.

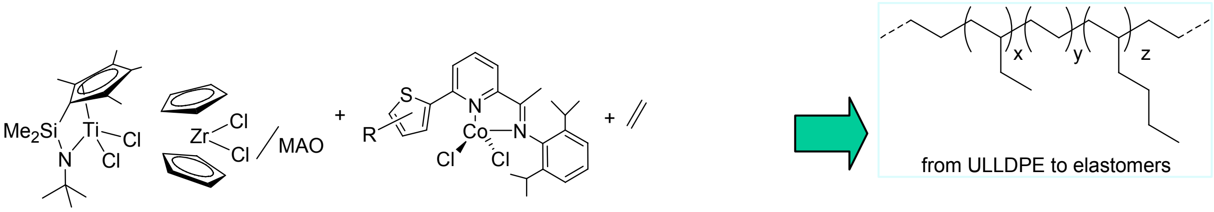


1 M = Sc, R = Me, L = THF
2 M = Sc, R = Ph, L = THF
3 M = Sc, R = C_6F_5, L = THF
4 M = Sc, R = 2-py, L = 2-py
5 M = Y, R = C_6F_5, L = THF
6 M = Lu, R = C_6F_5, L = THF

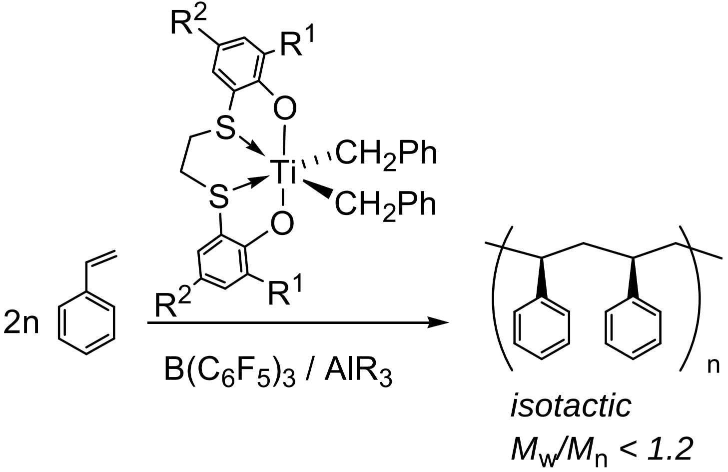
Design of Pd^{II} complexes with diphosphine ligands or new hemilable anionic P-O ligands has been achieved for the strictly alternating CO-olefin copolymerization as well as extra-insertion of ethylene units into the polymeric chain to yield polyketones of various chain lengths and the non-alternating CO-olefin copolymerization respectively.

Strategies for support of catalysts on the surface of tectons and in-situ polymerisation experiments in the presence of inorganic filler material have been evaluated and revised.

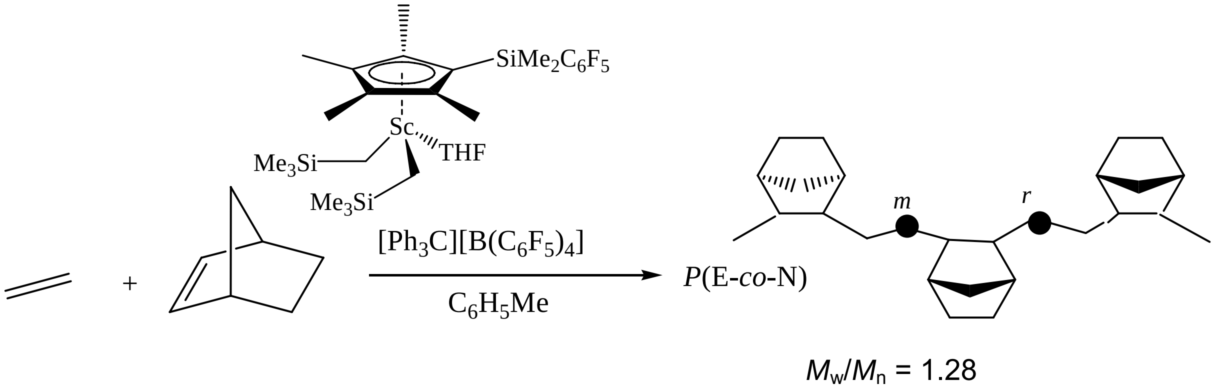
Homogeneous tandem catalysis using combinations of Co^{II} and Fe^{II} (bis)-imino(pyridyl) complexes in the presence of MAO has been achieved for the production of a variety of branched polyethylenes, spanning from semicrystalline LLDPE to completely amorphous, rubbery PE. Novel LDPEs with exclusively ethyl branches have been produced by tandem catalysis.



The living isospecific styrene polymerization by using a postmetallocene catalyst system developed is an important milestone achieved. The catalyst is derived from a bisphenolato metal complex. The presence of a bulky ortho-substituent in the ligand framework is necessary to ensure both activity and selectivity.



The living character of the ethylene (E)-norbornene (N) copolymerization has been demonstrated with scandium dialkyl catalysts [(η^5-$C_5Me_4\{SiMe_2R\})Sc(CH_2SiMe_3)_2(THF)$] with R = Me (**1**), C_6F_5 (**2**) as dimethylsilyl-substituents on the cyclopentadienyl ring, as precatalysts and $[Ph_3C][B(C_6F_5)_4]$ as activator. Both catalytic systems are extremely active, give alternating streoiregular copolymers, which can reach very high molar masses. The introduction of the bulky weak electron-with-drawing group C_6F_5 on silyl substituent of cyclopentadienyl ligand improves the controlled character of the copolymerization reaction by scandium systems. Kinetics experiments revealed that E-N copolymers yield and molar masses with rare catalyst **2** grow with time. This discovery is another important milestone in the achievements of the planned objectives. A series of polymers based on E, N and 2-hydroxymethyl-5-norbornene (**N$_{OH}$**) with several architectures have been achieved with catalyst $[Sc(\eta^5\text{-}C_5Me_4SiMe_3)(\eta^1\text{-}CH_2SiMe_3)_2(THF)]$ and $[Ph_3C][B(C_6F_5)_4]$ as cocatalyst: random copolymers such as *poly*(E-*co*-**N$_{OH}$** *)* *poly*(E-*ter*-N-*ter*-**N$_{OH}$**) with high yield, molar masses, and comonomer content which show good adhesion properties to polar substrates. *block copolymers such as **poly**(**E-co-N**)-**block-poly**(**E-ter-N-ter-N$_{OH}$**) **and poly**(**E-co-N$_{OH}$**)-**block-poly**(**E-alt-N**).*



Zinc-terminated oligomers were synthesized and functionalized in situ by exposure to CO_2, synthetic air or bromine. The hydroxylated polyolefins were successfully tosylated, the tosylated poly(ethene-*co*-1-hexene) can act as a macroinitiator to polymerize phenyoxazoline. The synthesis of **poly(ethylene-*block*-L,L-lactide)** was accomplished by using hydroxyl-terminated polyethylene as macroinitiator for the $Sn(Oct)_2$ mediated polymerization of L,L-lactide.

Polyethylene/layered silicate nanocomposites were successfully synthesized using PE-Py both as compatibilizer and modifier for the ME silicate. Great exfoliation has been achieved in PP/Montmorillonite nanocomposites prepared by using PP functionalized with MAH, and with PP functionalized with furane and MAH. The greatest exfoliation has been achieved by using a functionalized PP sample with higher molecular weight and functionalization degree.

MWCNT, with a carbon purity as high as 90 %, in a reproducible manner are produced by NANOCYL. Non-purified multi-wall carbon nanotubes/HDPE concentrates (50 % HDPE for most) were produced by polymerization filling-technique in a reproducible manner with controlled morphologies and coating ratio.
Some key-chemical modifications of carbon nanotubes were carried out at UMH and led to the homogeneous surface-functionalization of carbon nanotubes with relatively high content in reactive functions (e. g., amine).

Micro wave-assisted
cold plasma technique.
device used at UMH

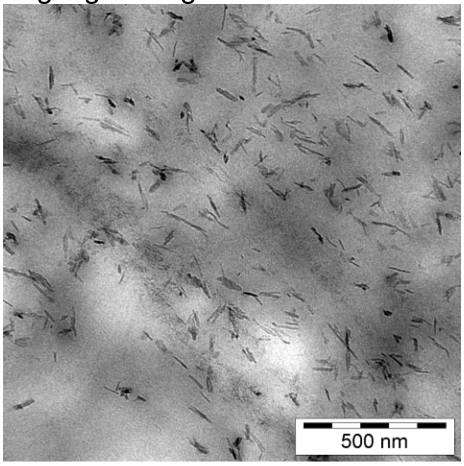
As far as the *in situ* (co)polymerization of ethylene or ethylene/2-norbornene or ethylene/1-hexene onto the surface of carbon nanotubes by using the polymerization-filling technique is concerned, some PE- E/N-,and E/H-coated nanotubes were produced and led to their deaggregation. These coated MWCNTs were then used as “masterbatches” for the preparation of finely dispersed polymer nanocomposites (i.e., EVA, HDPE, PP and PA6). As a result of the fine and homogeneous nanodispersion of a tiny amount of such coated MWCNTs (a few weight percents) in ethylene-*co*-vinyl acetate copolymer, polypropylene and polyamide-6 matrices by melt processing, mechanical and thermal properties of the material proved to be significantly enhanced (i.e., delay in the thermally induced degradation). The fire retardant and electrical properties of these polymer-based nanocomposites display also interesting results.

A new methodology for preparing of poly(E-N)/MWCNT nanocomposites was established by using a catalyst system which does not require MAO as cocatalyst. Poly(E–N)/MWCNT, poly(E–NOH)/MWCNT nanocomposites and poly(E–ter–N-ter-NOH) / MWCNT nanocomposites have been prepared with $[Sc(C_5Me_4SiMe_3)(CH_2SiMe_3)_2(THF)]$ catalyst and $Ph_3CB(C_6F_5)_4$ as cocatalyst in toluene solution. The TEM images of the nanocomposites obtained reveal the presence of areas with MWCNT covered by copolymers.

New nanocomposite materials have been prepared by the combination of the polymerization-filling technique (PFT) with tandem co-polymerization catalysis. This approach, which has proved to be a real breakthrough for controlling the microstructures of the growing polyolefin chains at the nanofiller surface, has been successfully applied to the homogeneous surface-coating of multi-walled carbon nanotubes (MWCNTs) with linear low-density polyethylenes (LLDPEs). Hybrid organic-inorganic materials have also been prepared by the in-situ strictly alternating and non-alternating CO-ethylene copolymerization onto silica-alumina based particles.

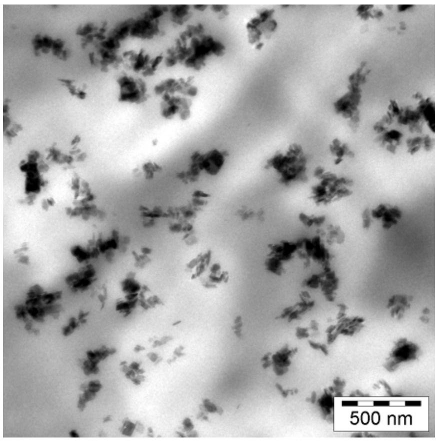
Sasol has produced a great variety of different organically modified and non-modifed boehmite aluminas (DISPERAL®). The variations ranged from different organic modifiers to different crystals shapes and sizes and as well different drying technologies. It was found that spray drying is an appropriate drying technology to produce nano dispersible aluminas. At the different partners extensive dispersing tests and mechanical tests were performed. With both methods, in-situ polymerization and melt compounding, were nanocomposites obtained.

In situ (co)polymerisation by means of Metallocene/MAO and postmetallocene/MAO catalysts anchored on the surface of novel boehmite nanofillers afforded new polyolefin hybrid materials. Various nanocomposites with low filler contents (< 10 wt.-%) and highly filled masterbatches (> 40 wt.-% filler) were prepared. The in situ olefin polymerization afforded very effective deagglomeration of boehmites. *In situ* olefin polymerization effectively reduces the strong boehmite nanoparticle interactions and improves in-situ formation and dispersion of boehmite nanorods. Melt extrusion of masterbatches containing easy-to-disperse nanoboehmites resulted in increased stiffness of HDPE and Engage without sacrificing high elongation at break.



TEM image of HDPE containing 8 wt.-% DISPERAL X-O prepared by in-situ polymerization.

Novel isotactic polypropylene (iPP) nanocomposites were prepared by melt-compounding using nanometer-sized boehmite AlO(OH) (DISPERAL®) with different crystallite sizes (10, 20, 40, 53 and 60 nm) and different acid surface modification (HSA, HBA, UA and OS2) as filler. Mechanical investigations of unmodified boehmite showed matrix reinforcement combined with impact strength improvement. TEM images evidenced a good dispersion of the nanofiller within the matrix without the application of any compatibilizers.



TEM image of iPP containing 10 wt.-% DISPERAL40 prepared by melt compounding.

Thermal analysis by means of DSC revealed that boehmites (unmodified, HSA-, HBA- and UA- modified) are able to act as nucleation agents for iPP which was visualized by means of polarized light microscopy and AFM. In contrast, at contents below 10 wt.-% OS2 with boehmite crystallite sizes of 40 and 60 nm down iPP crystallization ("anti nucleation"), reduced crystallization temperature and produced nanocomposites with significantly larger elongation at break and strain induced crystallization. As evidenced by scanning and transmission electron microscopic studies on strained iPP/OS2 nanocomposites, enhanced elongation at break was accompanied by multiple voiding and fibrillation of the strained matrix ligaments between OS2 nanoparticles.

Nanocomposites of iPP/EPDM blends (80/20) based upon unmodified and OS2 modified boehmites showed higher toughness expressed by an increase of notched impact strength values.

Boehmite nanoparticles were organically modified through a surface coating process based on ATRP polymerization in-situ of methacrylates. The proposed methodology allows to modulate the amount and type of organic polymer covering the inorganic surface. The modified Boehmite particles were tested for preparing polypropylene composites, which showed a good degree of interaction at the clay-polymer interface.

Two different organo-hydrotalcites were prepared by replacing carbonate anions of a synthetic hydrotalcite with dodecylbenzene sulfonate (DBS) and styrene sulfonate (SS) anions, respectively, through the method of the reconstruction of calcined-hydrotalcite. Polypropylene/DBS-hydrotalcite composites showed a heterogeneous intercalated/exfoliated morphology. The addition of a commercial compatibilizer caused the formation of intercalated-flocculated domains or even 3-D structures. Thermal properties were enhanced and material stiffness improved. Polystyrene/SS-hydrotalcite composites with different composition were prepared by free radical styrene polymerization in-situ. The composite with the lowest amount of clay was selected as material for the production of MOEMS sensor prototypes in WP5 (CRF).

The composition of the PP/MWCNT and PP/Disperal composites (masterbatches) and spinning parameters were optimised to obtain the suitable rheological properties for spinning as well as enhanced tensile strength and Young's modulus of composite fibres. The effect of reactive and non-reactive additives (compatibilisers, surfactants) was investigated. The PP composite fibres with improved mechanical properties (tensile strength up to 8.0 cN/dtex and Young's modulus up to 90 cN/dtex) and also with electrostatic properties (electrical conductivity about 10^{-5} S/cm) were prepared. The composite fibres exhibited higher UV barrier properties and acceptable light and thermal stability.

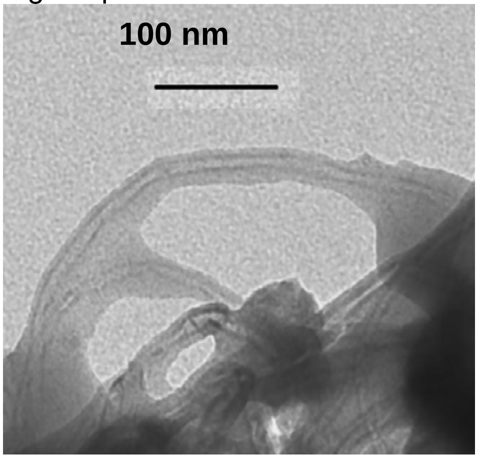
Nanocomposites were made adding different fire-retardant in the formulations. The polymers used were polyethylene, poly-1-butene and polypropylene. The nanofillers tested were MWCNT and various boehmites. Fire-retardants were hindered amine, zirconium phosphate, nanostructured polyphosphazene and zinc di (tri phenyl phosphonium). The nanofillers were homogenously dispersed in the different polymer matrices. The addition of fire retardant does not influence the dispersion quality. The fire retardant properties were investigated in WP4.

MWCNT covered by a thin homogeneous or textured PE layer were produced depending on the catalyst system (catalyst+co-catalyst). By applying the PFT to the copolymerization of different monomers, ethylene/2-norbornene and ethylene/1-hexene copolymers layers, were successfully obtained. Fine-tuning of the norbornene content in the copolymer produced depending on the experimental conditions was possible. In situ terpolymerization of ethylene/1-hexene/1,7-octadiene onto the surface of carbon nanotubes leads to the production of E/H/D-coated nanotubes.

Nanocomposites with a good dispersion of the fillers in the polymer matrices (PE, *i*PP, PA6, EVA, PLA) were produced by melt processing the PE, P(E-*co*-N)- and P(E-*co*-H)-coated nanotubes. The obtained material showed a significant improvement of the properties in terms of mechanical and fire retardant properties.

Depending on the catalyst system used, it was evidenced by TEM that the MWCNTs are covered by a homogeneous or a textured polymer layer (i.e., nanohybrid “sausage”- and “shish-kebab”-like structure, respectively) and completely separated from the starting bundle-like associations. The fine dispersion of PE-, E/H- and E/N-coated MWNTs *via* the “masterbatch” process in various polymer matrices (i.e., EVA, *i*PP, HDPE, PA6 and even biodegradable PLA) leads to an improvement of the mechanical and thermal properties such as a significant increase of the Young’s modulus for materials filled with 6 wt.-% of fillers or a delay in the degradation of the composites with respect to the neat matrix, respectively. Moreover, the electrical properties of EVA-based nanocomposites were investigated by measuring the change in volume resistivity with a significant drop in resistivity achieved for a percolation threshold of less than 2 wt.-% and a plateau for nanocomposites containing 3 wt.-% of filler. The flame retardant properties as well as the photodegradation of EVA-based nanocomposites were investigated by Cone calorimetry and UV ageing, respectively. As a result, the final properties of the resulting material show a significant improvement as compared to neat EVA matrix (i.e., formation of a cohesive residues and stabilisation of the polymers upon heating due to the addition of PE-coated MWCNTs).

The synthesis of poly(E–co–N) / MWCNT nanocomposites, poly(E–co–N_{OH}) / MWCNT nanocomposites and poly(E–ter–N-ter-N_{OH}) / MWCNT nanocomposites using a catalyst system which does not require MAO as cocatalyst seems to give very interesting results. One advantage is that no MAO residues are contained in the nanocomposites. TEM images reveal the wrapping of the the poly(E–co-N), poly(E–co–NOH) and poly(E–ter–N-ter-N_{OH}) on a good part of the MWCNTs.



Boehmites show an increase in fire-retardants properties and thermal stabilization. Moreover MWCNTs show encouraging results, nanocomposites with LLDPE and PP maintain good characteristics also at low concentration of filler. The mechanism of thermal stabilisation of MWCNTs in LLDPE was evidenced; a similar one was postulated for PP/MWCNTs nanocomposites. Some fire retardants show very good behaviour to fire test however the formulations need some adjustment in order to achieve an UL-0 behaviour.

OS1 and OS2 nanofiller from Sasol show high electrical and optical properties and are promising candidates for the application in thin film nanocomposites (the same trend is also available for NTCs). The increasing of dielectric constant obtained with novel nanohybrids allowed selecting the best materials: *in situ* PS with low percentage of hydrotalcite and PE-N with 5-10% of OS1. These materials will be used to the production of the final MOEMS sensor prototypes in WP5.

Mechanical properties of PE/Dispersal hybrid materials like Young's Modulus and yield stress could be improved without the expense of high elongation at break. It could be shown that melt compounding "masterbatches" resulted in improved mechanical properties compared to conventional melt compounding. This is attributed to the improved dispersion when masterbatches are produced by *in situ* polymerization.
HDPE nanocomposites based on boehmites with variable aspect ratio (Nanorods and nanoplatelets) were analyzed by means of TEM and stress strain measurements. The *in situ* olefin polymerization afforded very effective deagglomeration of boehmites. Melt extrusion of masterbatches containing easy-to-disperse nanoboehmites resulted in increased stiffness of HDPE without sacrificing high elongation at break. Mechanical performance improved with increasing aspect ratio of the nanoboehmites only when effective boehmite deagglomeration was achieved. The *in situ* olefin polymerization with small boehmite content of around 4 wt.-% afforded very effective nanorod filler dispersion and improvement of mechanical properties. It is obvious that the anchoring of catalysts on the boehmite surface and the *in situ* olefin polymerization between the nanoboehmites very effectively reduces the strong boehmite nanoparticle interactions and improves deagglomeration and *in situ* formation and dispersion of boehmite nanorods.

The optimal composition of PP composite fibres and preparation (spinning and drawing) conditions were defined. The unambiguous proportional straight-line dependence between tensile properties (tenacity, Young's modulus) of the PP and PP composite fibres and average melting temperatures (T_p and T_{ma}) obtained by DSC CLM method was found. The CLM method could be utilised for characterisation of the convenient supermolecular structure of the spun fibres for deformability in drawing process and tensile properties of drawn fibres.
It was found that treated Disperals DUN and DAM effect less negatively on light stability of PP in comparison with Disperal 40. The significantly higher light stability was evaluated for all kinds of investigated fibre forming PP. In contrast to Disperals, the MWCNTs in PP increase stability of PP molecular weight under UV radiation. The Disperal nanoparticles negatively affect the thermo oxidation stability of the PP/Disperal composites. The PP samples with content of treated Disperal DAM degraded extremely fast. The PP/D40, PP/D60 and PP/DUN composites degraded slowly. The relative higher thermooxidation stability was evaluated for PP/MWCNT composites.

Thermo-oxidation and photo-oxidation of solid nanocomposites with carbon nanotubes and nanoclays have been studied. Carbon nanotubes stabilize the PP matrix during thermo-oxidation ageing and for the photo-oxidation. Propagation reactions decrease and/or initiation-termination reactions increase. Alumina reduces the life-time of nanocomposites and affects both the induction period and rate of oxidation. This comportment is opposite to carbon nanotubes which stabilizes the nanocomposites and affects only the induction period. The concentration of CNT influences to first order the increasing of life time. Preparations of

CNT as coating, cutting, purification or functionalization influence the ageing only to second order.

The fabrication process of the MOEMS device has been optimised introducing the OS1 nanofiller, the increasing of dielectric constant allows reducing the gap between SiO and PS/OS1 (10% charge) to values less than 20%.
The realization of an automotive component (interior trim) made of polypropylene (PP) by injection moulding process has been optimised.

The PP composite fibres with improved mechanical properties were prepared. The tenacity and the dynamic modulus of PP/MWCNT composite fibres and of PP/Disperal 40 composite fibres were enhanced about 50-100% compared to unmodified fibres.
PP/MWCNT composite fibres prepared have also excellent barrier properties and thermal stability. Barrier properties of PP/Disperal fibres were enhanced more than 50% for concentration of solid particles up to 3.0 wt%. Thermal stability of PP/Disperal composite fibres can be improved using common thermal and light stabilisers.

Based on the developed activity the best performing nanofillers have been selected and the appropriate formulation has been tuned in order to produce nanocomposites based on different polyolefinic grades (e.g. homopolymer, heterophasic copolymer, etc…)
the nanofillers all can provide an increase in flexural elastic modulus (FEM) and heat distortion temperature (HDT) but the best performance is with no doubt expressed by the Cloisite 15A from Southern Clay Product (50% enhancement of FEM) closely followed by the Dellite 67G from Laviosa Chimica Mineraria (35% enhancement of FEM).

Perspectives

The NANOHYBRID material will be of special interest for the upgrading and diversification of polyolefin compositions produced by transition metal catalyzed polymerisations. The production of polyolefin materials offers economical, environmental and application-oriented advantages:

- *Economical*: It is an important industrial sector accounting for more than half of the modern 200 million ton/year plastics production.
- *Environmental*: Polyolefins are prepared in highly effective catalytic processes requiring low energy and preserving the oil-like energy content of polyolefins. Upon heating above 300°C, the polyolefins degrade to recover synthetic oil and natural gas.
- *Industrial Applications*: as a function of catalyst type, process conditions, polymer processing and especially the type of olefin copolymer and functional fillers, it is possible to tailor a wide variety of materials which meet the demands of modern technologies ranging from packaging and low weight engineering materials to communication technology.
- *Application-oriented property enhancement, thanks to nanostructured hybrid polyolefins*. In the medium to long term, tecton and hybrid approaches to advanced nanostructured polymers via catalytic polymerisation combined with block copolymer self-assembly will offer unique benefits and opportunities for new applications and products. Targeted enhanced properties are: scratch resistance, modulus improvement without sacrificing stiffness, heat distortion temperature, flame retardancy, barrier properties (super hydrofobic/hydrophilic, UV radiation, conductivity, antimicrobial, etc.). The industrial sectors concerned could be automotive, communication technology, MEMS, packaging, and textile.

Thus, specific industrial applications have been investigated with the aim to perform some preliminary studies on tailorisation of nanocompomers and nanocomposites in industrial applications.

GENERAL CONCLUSION

During the three years of activity, NANOHYBRID project was very successful in all aspects. The very good interactions among excellent partners with complementary expertise brought to significant new achievements as summarized above.

Fundamental knowledge to create new melt processable nanophase-separated hybrid materials with controlled architecture, derived from low cost olefins has been developed. This is testified from the great number of publications in JCR journals 54 of which 16 are published jointly among different partners. In addition results have been presented at International meetings on catalysis, processing …. ….

Novel nanoparticles have been created: i) organophilic inorganic polyelectrolyte nanoparticles (such as different doped and non-doped aluminas, silica-aluminas, and hydrotalcites to cover a wide range of surface acidities); ii) carbon nanotubes (such as well defined MWNT and DWNT, as well as functionalized CNTs.

Novel catalysts for living based on rare-earth metal bisalkyl half-sandwich complexes and homogeneous tandem polymerization, using combinations of Co^{II} and Fe^{II} (bis)-imino(pyridyl) complexes in the presence of MAO, have been created. These achievements allowed to create novel polymer architectures, novel random and block copolymers with polar and apolar blocks and polymer product compositions in order to improve matrix/filler adhesion and nanofiller dispersion.

Catalyst were supported on the tectons for in situ (filling) polymerisation to produce nanoparticles coated with polymer, which have been used intermediates to obtain novel nanohybrids with high inorganic content. Complex melt processable polyolefin hybrids have been designed. NANOHYBRID nanocomposites, with a very small amount (a few weight-percent) of nanometer-scaled anisotropic tectons, combining chemical and physical bonding between nanofiller and matrix have obtained which is a real breakthrough in material's properties

Fundamental characteristics of the organic-inorganic interphase region of nanocomposites' have been investigated by multi-scale analysis either during in-situ polymerisation or during melt processing. Such an understanding and its dependence on nanoelement surface chemistry, the relative arrangement of constituents and, ultimately, its relationship to polymer nanocomposite properties, that is the hybrid material behavior, can be considered a research frontier in this field.

Examples of enhanced properties are:

i) Mechanical properties of PE/Dispersal hybrid materials like Young's Modulus and yield stress could be improved without the expense of high elongation at break;

ii) an increase in flexural elastic modulus (FEM) and heat distortion temperature (HDT) the best performance is with no doubt expressed by the Cloisite 15A from Southern Clay Product (50% enhancement of FEM)

iii) Electrical properties of Nano-composite with CNT increase the electrical conductivity with only 0,2% of CN.

Among the various applications which have been explored in order to assess the capabilities of the NANOHYBRID material those that may be further developed to industrial processes in the medium to long term are:

- *Materials design for automotive parts*:The realization of an automotive component (interior trim) made of polypropylene (PP) by injection moulding process has been optimised.
- *Advanced functional materials for communication technology*
- *Advanced functional materials for high performance elastomers*
- *Polymer MEMS (micro-electro mechanical system) components*:The fabrication process of the MOEMS device has been optimised introducing the OS1 nanofiller.

-Nanocomposite polyolefin fibres for textile

There was no deviation in the submission of the deliverables. No problems or change in responsibilities was encountered during the same period.

Website www.nanohybrid-project.com

Consortium

The consortium of the NANOHYBRID project involves top scientists from 3 national research centres, 5 academics, 3 industrial technology providers and 2 end users.

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