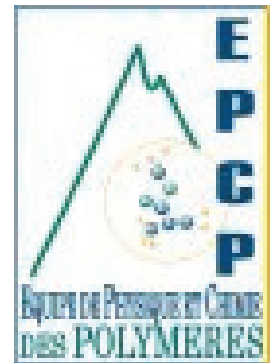


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STATE OF THE ART THERMOPLASTIC NANOCOMPOSITES





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1 SCOPE

Methodology of the state of arts thermoplastic nanocomposites

A lot of thermoplastic matrix for the nanocomposites :

- Focus on the thermoplastics used in automotive and mechanical industries

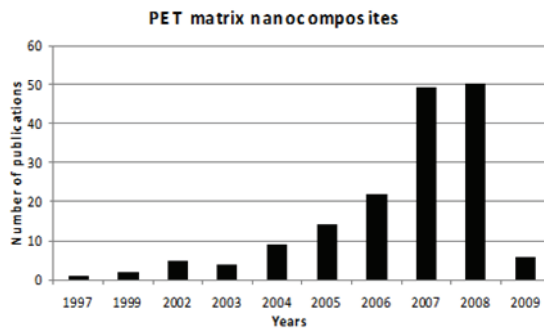
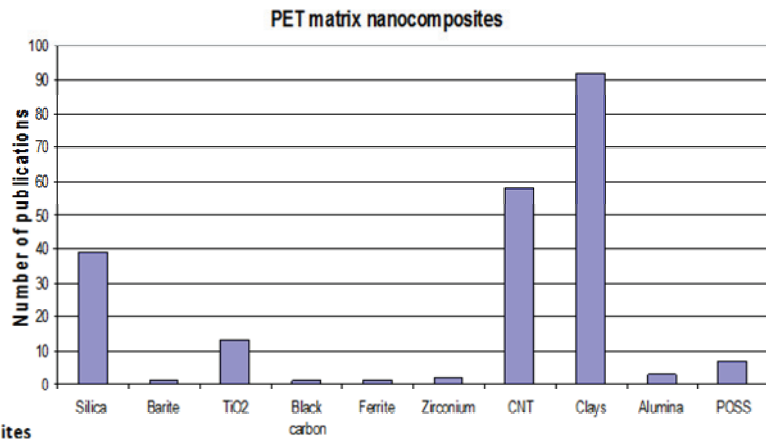
PET, PA, PP

1°) Research PET, PP, PA matrix nanocomposites and find the nanocharges used

2°) Research studied properties for each matrix and principal nanocharges

PET matrix nanocomposites

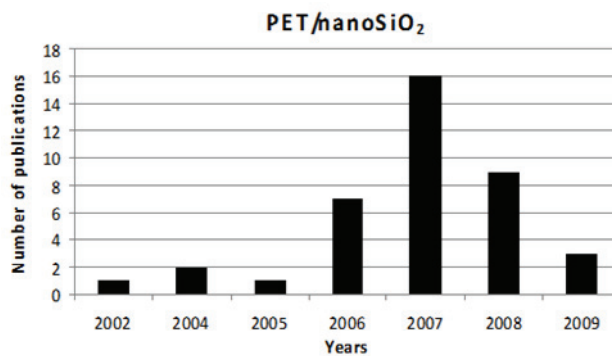
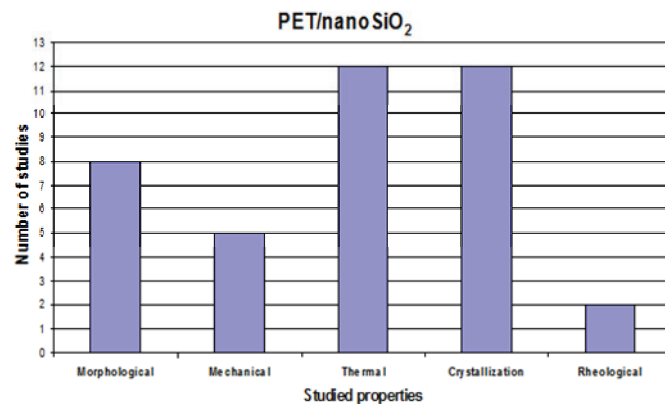
Keywords :
PET and nanocomposites



Nanocharges

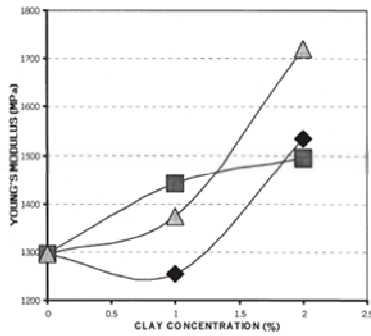
PET matrix nanocomposites and nanosilica

Keywords :
PET and nanocomposites and silica

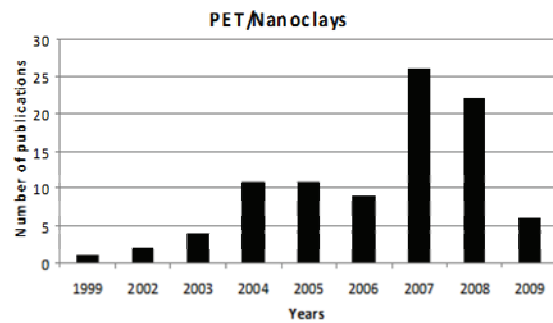
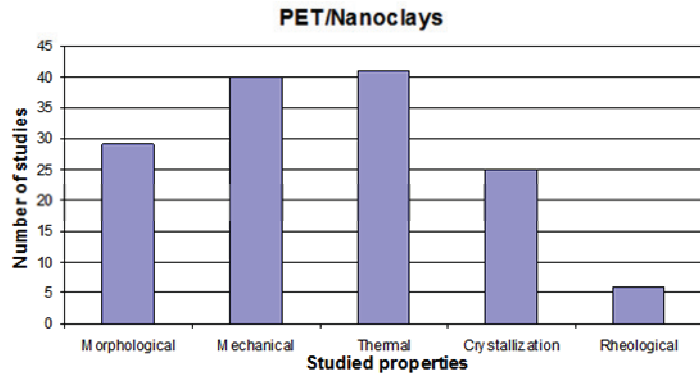


PET matrix nanocomposites and nanoclays

Keywords :
PET and nanocomposites and clays

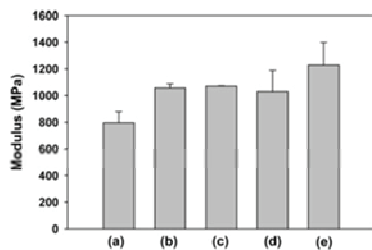


Variation of Young's modulus with montmorillonite concentration
Production of nanocomposites of PET/montmorillonite clay by an extrusion process – 2003 Macromolecular Symposia



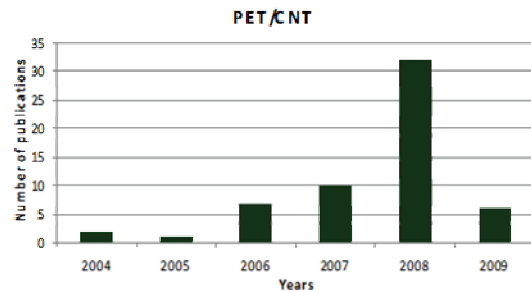
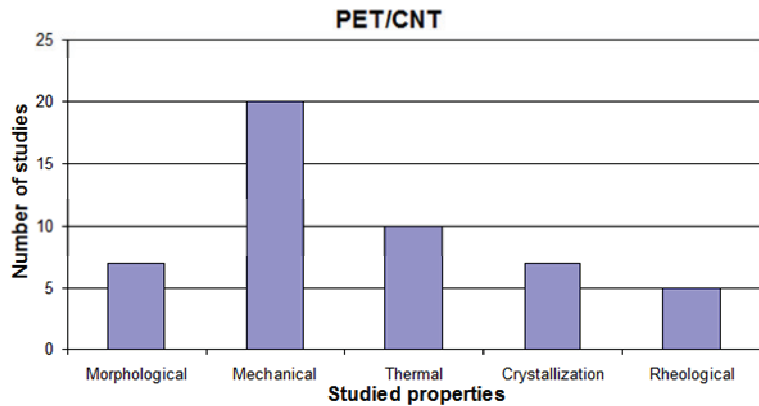
PET matrix nanocomposites and carbon nanotubes

Keywords :
PET and nanocomposites and carbon nanotubes



Modulus of pure PET and nanocomposites.
 (a) PET, (b) PET/MWNT, (c) PET/MWNT-COOH,
 (d) PET/MWNT-benzyl, and (e) PET/MWNT-phenyl

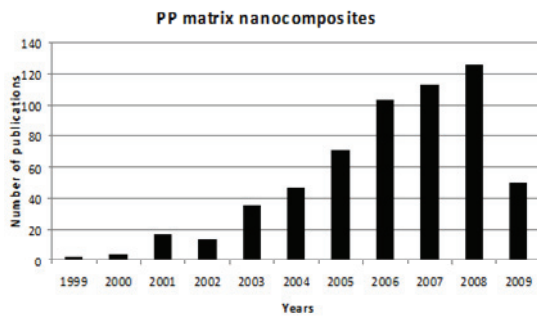
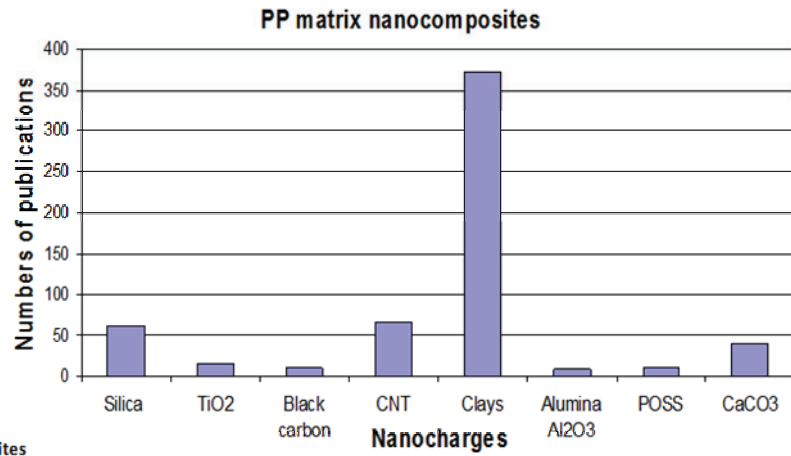
Effect of interaction between poly(ethylene-terephthalate) and carbon nanotubes on the morphology and properties of their nanocomposites – 2008 Journal of Polymer Science



PP matrix nanocomposites

Keywords :

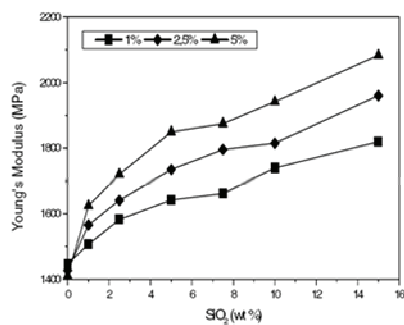
PP and nanocomposites



PP matrix nanocomposites and nanosilica

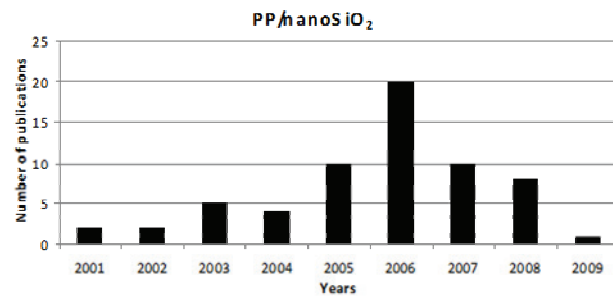
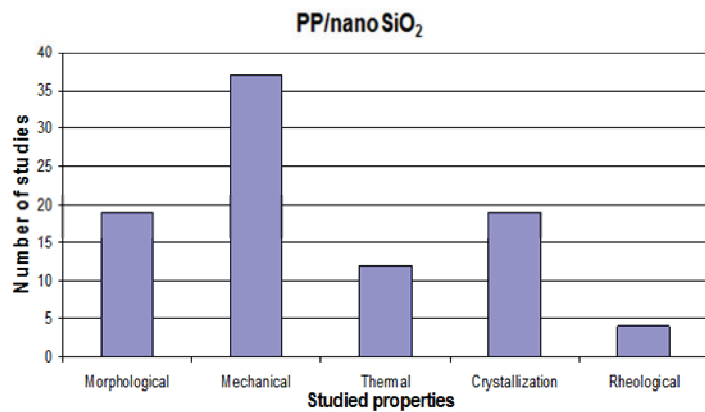
Keywords :

PP and nanocomposites and silica



Variation of Young's modulus with SiO₂ concentration

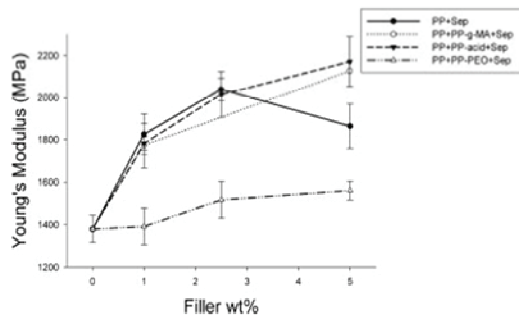
Mechanical properties and morphological examination of isotactic Polypropylene/SiO₂ nanocomposites containing PP-g-MA as compatibilizer - 2005 Journal of Physics



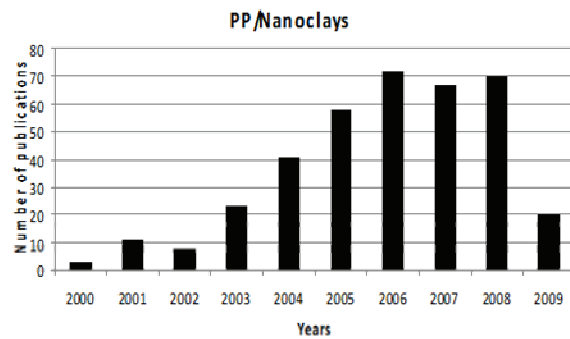
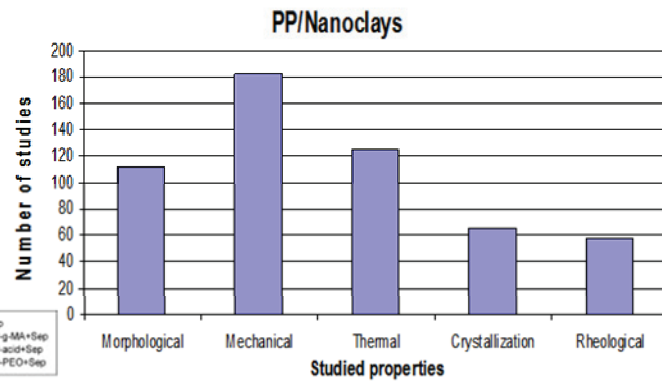
PP matrix nanocomposites and nanoclays

Keywords :

PP and nanocomposites and clays



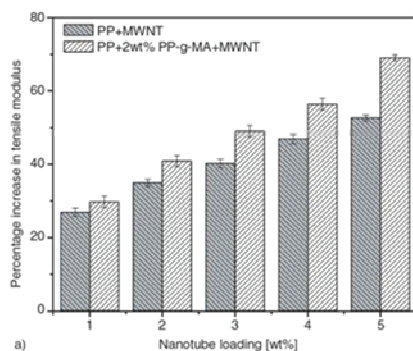
Variation of Young's modulus with sepiolite concentration
Polymer Nanocomposites Based on Needle-like Sepiolite Clays: Effect of Functionalized Polymers on the Dispersion of Nanofiller, Crystallinity, and Mechanical Properties – 2006 *Journal of Applied Polymer Science*



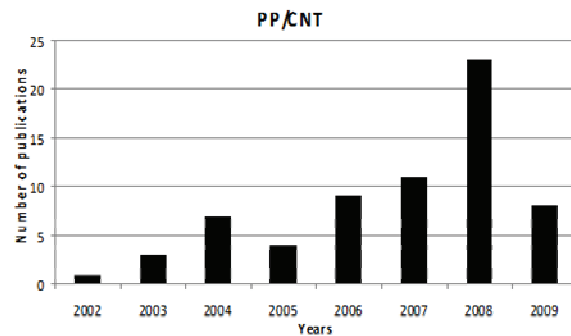
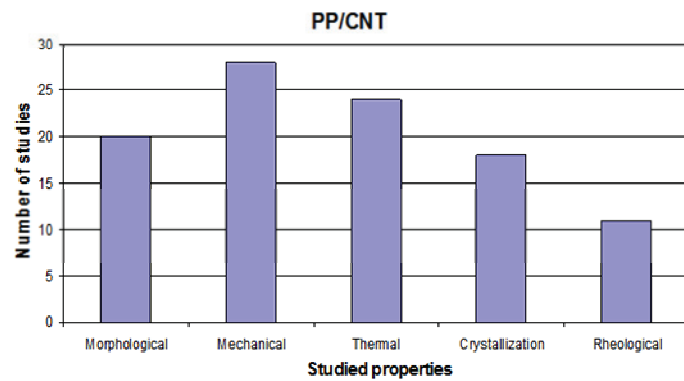
PP matrix nanocomposites and carbon nanotubes

Keywords :

PP and nanocomposites and carbon nanotubes



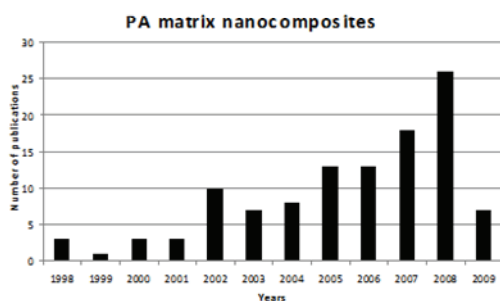
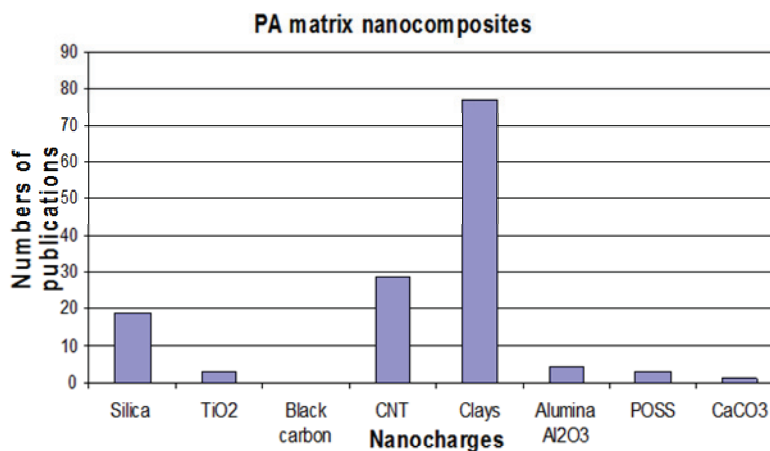
Percentage increase in tensile modulus with MWNT content for the PP/MWNT and PP/MWNT/2 wt% PP-g-MA composites
Multi-walled carbon nanotube filled polypropylene nanocomposites based on masterbatch route: Improvement of dispersion and mechanical properties through PP-g-MA addition – 2008 *EXPRESS Polymer Letters*



PA matrix nanocomposites

Keywords :

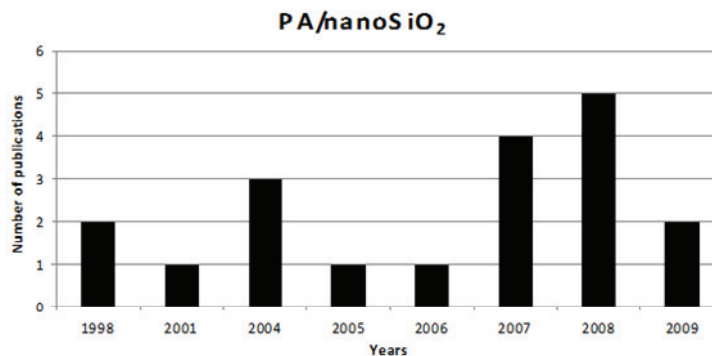
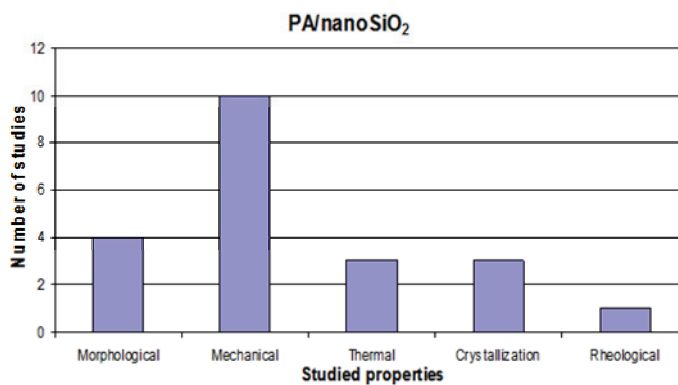
PA and nanocomposites



PA matrix nanocomposites and nanosilica

Keywords :

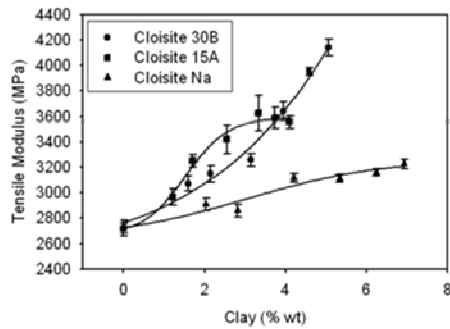
PA and nanocomposites and silica



PA matrix nanocomposites and nanoclays

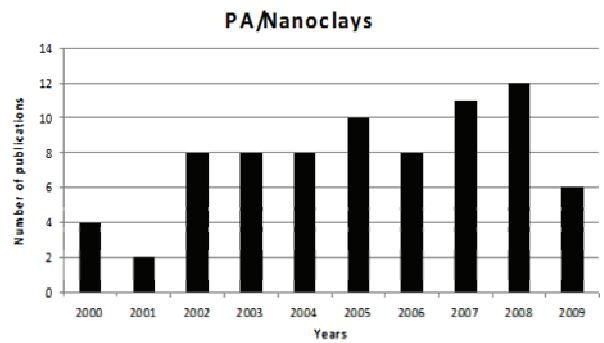
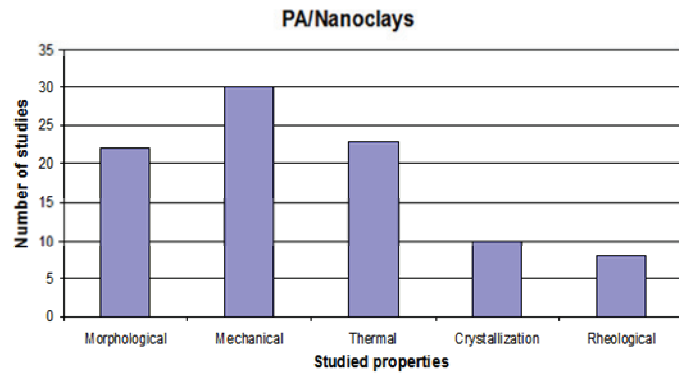
Keywords :

PA and nanocomposites and clays



Tensile moduli of PA-6 nanocomposites produced with different clays

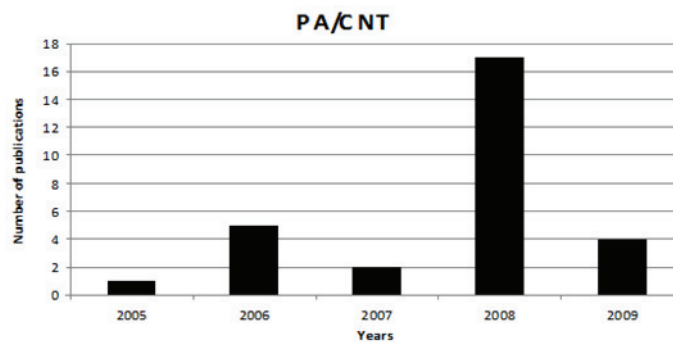
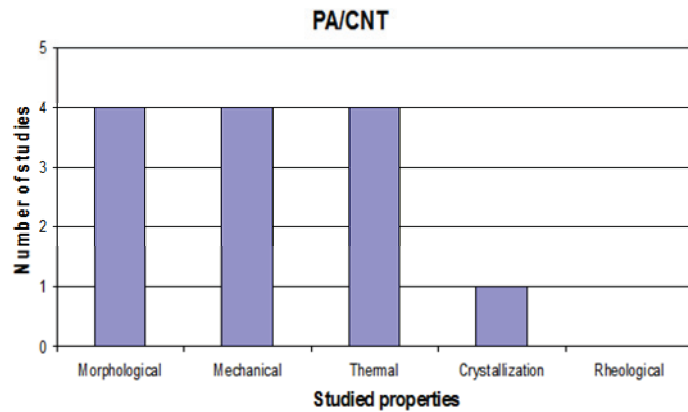
Melt Processing Effects on the Structure and Mechanical Properties of PA-6/Clay Nanocomposites - 2006 Polymer Engineering and Science



PA matrix nanocomposites and carbon nanotubes

Keywords :

PA and nanocomposites and carbon nanotubes



2 CONCLUSIONS

Because of the very numerous literature related to nanomaterials, it was decided to focus the scope of the study in composite materials with matrix used primarily by companies in the sectors targeted for transfer, machinery and mechanics systems. These matrix are poly (ethylene terephthalate) (PET), polypropylene (PP) and Polyamide (PA).

For each of the selected matrix (PET, PP and PA) was investigated the most commonly used nanoparticles and the characteristics of the materials.

As a result of this research has concluded that the most commonly used nanoparticles are the nanoclay, carbon nanotubes and nanosilica. On the other hand, the characteristics most investigated with the introduction of nanoparticles are mechanical properties, thermal properties and morphology.



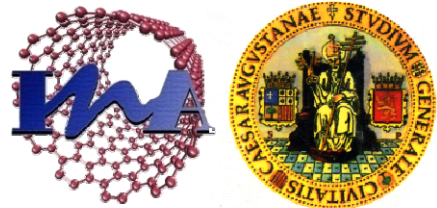
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Pau, September of 2009

BY UNIVERSITE DE PAU ET DESA PAYS DE L'ADOUR:

0001

**Seleccion of Nanoparticles to replace Glass
Fibers as fillers in PET composite materials**





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1 SCOPE

Layered silicate nanofillers have demonstrated enhanced properties in the polymers in which they are dispersed. Amongst those properties, an unexpectedly large increase in moduli (tensile or Young's modulus and flexural modulus) of nanocomposites with filler contents sometimes as low as 1 wt.% has drawn a lot of attention. Thermal stability and fire retardancy through char formation are other interesting and widely searched properties displayed by those nanocomposites. These materials have also been studied and applied due to their superior properties as barriers against gas and vapor permeation. Finally, depending on the type of polymeric materials, they can also display interesting properties in the frame of ionic conductivity or in the thermal expansion control [M. Alexandre, P. Dubois / *Materials Science and Engineering* 28 (2000) 1±63]. On the other hand, because of the special crystal structure of fibrous silicates, the interaction between different rod-like crystals is weak and a large amount of hydroxyl groups exists on the surface favoring the good dispersion of the fibers in the polymeric matrix [X. Yuan et al. / *Polymer Degradation and Stability* 93 (2008) 466-475].

The basic reason for selecting LDH for nanocomposites is their typical metal hydroxide-like chemistry and conventional clay-like layered crystalline structure. The former is helpful in the direct participation in the flame inhibition through endothermic decomposition and stable char formation. On the other hand, they have a layered structure with aspect ratios similar or even higher than that observed for aluminosilicates, making LDH suitable for polymer nanocomposite preparation. In recent years, polymer/LDH nanocomposites have attracted a great interest because they exhibit improved physical and performance properties in comparison to the pristine polymers and conventional composites [S.P. Lonkar et al. / *Polymer* 50 (2009) 1505–1515]. LDH modified with an anionic surfactant: dodecylsulfate (DS) provided good compatibility with PET molecules, resulting in exfoliated LDH-DS/PET nanocomposites having enhanced thermal and mechanical properties as compared to homo PET [W.D. Lee et al. / *Polymer* 47 (2006) 1364–1371].

Single-wall carbon nanotubes (SWCNT), multi-wall carbon nanotubes (MWCNT) and carbon nanofibers (CNF) have attracted much attention since their discovery. Their exceptional mechanical, electrical, thermal properties and high aspect ratio make them excellent candidates as fillers in multifunctional nanocomposites. The characterization of the mechanical properties and fatigue tests have been performed on PET control and PET-CNF samples [R.D. Averett et al. / *Composites: Part A* 40 (2009) 709–723]. In most cases, for the unfatigued samples the PET nanocomposite (PET-CNF) sample exhibited superior mechanical properties. But the composites showed greater deterioration in the mechanical properties as a result of fatigue compared to PET. In sum, the results from this study indicate that PET unreinforced samples can withstand a larger accumulation of strain from the fatigue process conducted at the same maximum stress level as compared with the PET-VGCNF nanocomposite samples. Single walled carbon nanotubes dispersed in PET through the ultrasound assisted solubilization route have been shown to act as effective nucleating agents for PET crystallization. As expected, SWNTs are also shown to impart electrical conductivity to the PET matrix, with a percolation threshold at SWNT concentration of 1 wt% in PET matrix. Analysis of the mechanical properties reveals that



small fractions of SWNTs can substantially reinforce PET [Anoop Anand K et al. / European Polymer Journal 43 (2007) 2279–2285].

Several nanoparticles have been used as fillers to reinforce PET. To improve the properties of Poly(ethylene terephthalate) in thermal stability and barrier to water, nano-SiO₂/PS composites were prepared and their water absorption and thermal stability behaviors were investigated [T. Wu, Y. Ke / Polymer Degradation and Stability 91 (2006) 2205e2212]. It was found that nano-SiO₂ particles in PET play a barrier to both water and oxygen and may delay the degradation of PET in heating processing. It was reported that wear resistance of PET increases nearly 2X with the addition of 2 wt.% 38 nm alumina particles. Wear resistance of PET increases with the addition of nanoparticles at low loadings irrespective of the crystallinity of the polymer matrix. The improvements in wear characteristics are attributed to the formation of a more coherent and adherent transfer film by the nanofilled composites [P. Bhimaraj et al. / Wear 258 (2005) 1437–1443].

According to the revision of the existing literature (ISI web of knowledge) the nanomaterials used as fillers in PET composites can be separated in three families: i) layered nanofillers, ii) carbon-based nanomaterials, iii) inorganic nanoparticles.

Some used examples are as follows:

i)

- Montmorillonite

Cloisite® 10A, Cloisite® 15A, Cloisite® 20A , Cloisite® 30A (Southern Clay Products).

Nanofil 15 (SÜD-CHEMIE Co., Germany)

MM modified with: octadecyltrimethylammonium chloride .

hexadecyltrimethyl ammonium bromide.

(4-carboxybutyl) triphenylphosphonium bromide

12-aminododecanoic acid (ADA).

Dodecyltriphenylphosphonium

- Hectorite

SOMASIF MAE (synthetic fluorhectorite modified by dimethyl tallow quaternary ammonium ion, provided by CO-OP Chemical Co., Japan)

- Dodecyltriphenylphosphonium-mica.

- 1-hexadecane benzimidazole-mica

- Bentonite

Bentone® 2010 (Elementis Specialties)

oligostyrene-modified bentonite

- Fibrous palygorskite, sepiolite and chrysotile

- Layered double hydroxide (hydrotalcite, modify using dodecylsulfate (DS), dodecylbenzenesulfonate (DBS), and octylsulfate(OS) by rehydration process).

ii)

- MWCNT

- SWNT

- Carbon nanofibers



iii)

- SiO₂
- TiO₂ (UV-blocking)

- ATO (antimony doped tin oxide) (anti-static electricity properties).
- Al₂O₃

2 CONCLUSIONS

Recommendation:

We could start with Al₂O₃ which is demonstrated to increase the wear resistance, is commercially available, and not expensive. The second choice would be any layered clay, since they are intensely studied and they are commercially available even modified. Any carbon material would be also very interesting.



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Zaragoza, September of 2009

BY INSTITUTO DE NANOCIENCIA DE ARAGON

0002

NANOPARTICULES



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1 SCOPE

NANOPARTICULES FOR ENHANCEMENT OF PET'S MECHANICAL PROPERTIES

Comparaison between PETs from DSM

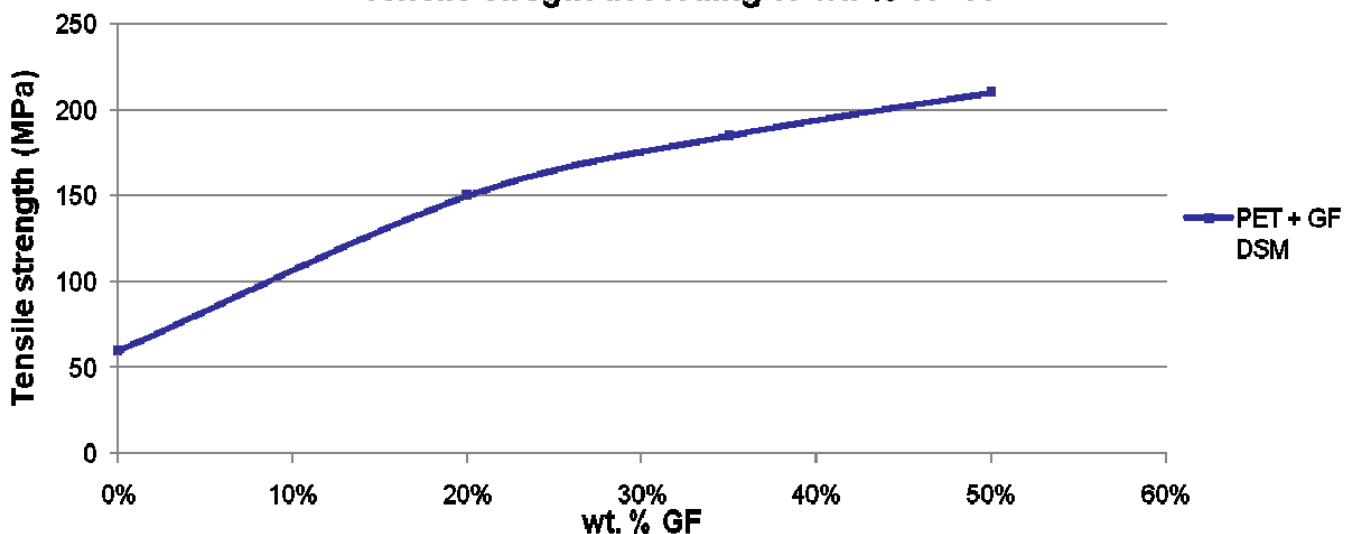
Glass Fiber wt.%	0%	20%	35%	50%
Grade name	Arnite® D04 300*	Arnite® AV2 340	Arnite® AV2 372	Arnite® AV2 390
Stress at break (MPa) (Campus)	60	150	185	210

Evolution of stress at break according to wt.% of Glass Fibers

	PET 0% -> 20% GF	PET 0% -> 35% GF	PET 20% -> 35% GF	PET 20% -> 50% GF	PET 35% -> 50% GF
Enhancement of stress at break (%) according to wt.% of Glass Fiber	+ 150%	+ 208%	+ 23%	+ 40%	+ 14%

Enhancement of tensile strength between PET+20% GF and PET+35% GF = **23%**

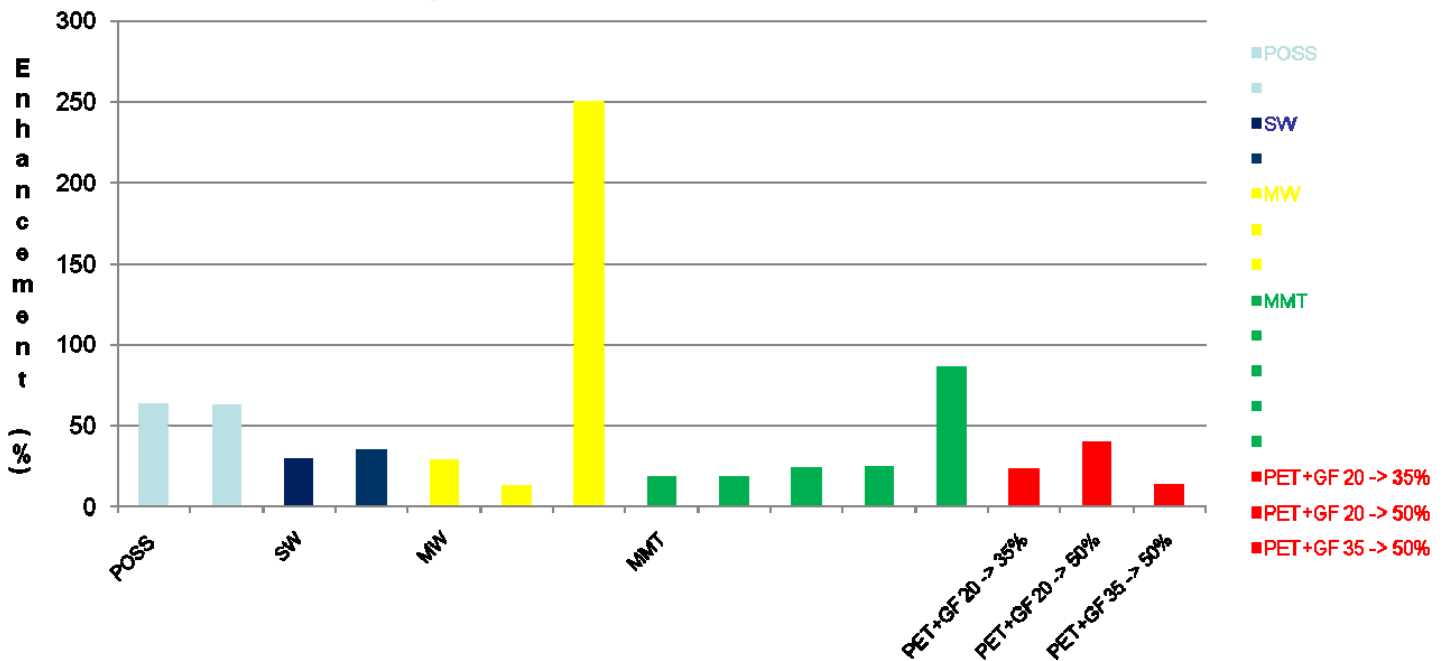
Tensile strength according to wt. % of GF



Comparaison between PETs from DSM and PET nanocomposites

	POSS		CNT			CLAYS					Arnite DSM				
			SW	MW		MMT					PET+GF 20 -> 35%	PET+GF 20 -> 50%	PET+GF 35 -> 50%		
Tensile strength (MPa)	50	50	55	37	49	69	150	59	61	65	68	52			
Enhancement (%)	63	63	30	35	29	13	250	18	18	24	25	86	23	40	14
wt. %	1	1	3	3	3	3	0,5	0,5	1	4,5	1	0,5	35	50	50
n° publis	62	61	41	49	42	47	52	3	8	25	28	31			

Enhancement of tensile strength for PET nanocomposites compared to pristine PET and PET+GF from DSM



Nanoparticules increasing PET nanocomposites tensile strength up to 23% compared to pristine PET :

- MMT (*n° publication :25, 28, 31*)
- SWCNT (*41, 49*)
- MWCNT (*42, 52*)
- POSS (*61, 62*)

N°	Periodic	Year	Autors	Nanocharge	%m	Modifiers	Process	Mechanical properties
<u>25</u>	Journal of Polymer Science	2008	GUOLI WANG, et al.	MMT	4,5		Solid state shear milling (S ³ M) + Twin-screw extrusion	$\sigma = 65$ MPa
<u>28</u>	Composites Engineering	2005	Yimin Wang, et al.	MMT	1		High speed mixer + Twin-screw extrusion	$\sigma = 68$ MPa
<u>31</u>	Journal of Applied Polymer Science	2007	Se Hoon Kim, et al.	MMT	0,5	N-methyl diethanol amine	In-situ polymerization	$\sigma = 52$ MPa
<u>49</u>	European Polymer Journal	2007	Anoop Anand K, et al.	SWCNT	3		Ultrasound assisted dissolution-evaporation method	$\sigma = 37,2$ MPa; E= 2,54 GPa
<u>41</u>	Journal of Applied Polymer Science	2007	Anoop Anand K, et al.	SWCNT	3		Melt-compounding + Compression molding	$\sigma = 54,9$ MPa ; E= 1,87 GPa
<u>42</u>	Journal of Polymer Science	2008	HYE JIN YOO, et al.	MWCNT	3	benzyl isocyanate and phenyl isocyanate	Twin-screw extrusion	$\sigma = 49$ MPa; E= 1,2 GPa
<u>52</u>	Journal of Applied Polymer Science	2008	Sang Hyun Jin, et al.	MWCNT	0,5	Acid and acetic group	In-situ polymerization	$\sigma = 150$ MPa ; E= 5 GPa
<u>62</u>	Journal of Applied Polymer Science	2008	Jang Kyung Kim, et al.	POSS	1	disilanolisobutyl and	In-situ polymerization	$\sigma = 50$ MPa; E= 4,5 GPa
<u>61</u>	Composites Science and Technology	2008	Hong-Un Kim, et al.	POSS	1	aminopropyl isobutyl and aminopropyl	In-situ polymerization	$\sigma = 50$ MPa; E= 4,2 GPa

2 CONCLUSIONS

LIST OF POSSIBLE NANOPARTICULES

MMT :

Advantages: - widely studied

- available commercialy without modifications
- good enhancement of mechanical properties

Disadvantages: - low thermal stability of modifiers during melt process

CNT (SW&MW):

Advantages: - good enhancement of mechanical properties

Disadvantages: - expansive

- fonctionnalization essential
- high toxicity

POSS :

Advantages: - very good enhancement of mechanical properties

- not much studied

Disadvantages: - fonctionnalization essential

- melt compounding possible?



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Pau, September of 2009

BY UNIVERSITE DE PAU ET DESA PAYS DE L'ADOUR:



2300_I090284

STATE OF THE ART IN PATENTS OF PET MATERIAL AND NANOPARTICLES



INSTITUTO TECNOLÓGICO DE ARAGÓN

Area of Research,
Development and
Technological Services



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2.3	<i>Third search: Goldfire database, strategies: PET + nanocomposite</i>	12
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1 OBJECTIVE

The aim of this report is to show the state of art in terms of patents in nanocomposites of PET matrix reinforced with glass fiber. The study is include in TECNA project and according to its objective the patent search is going to be focused in the mechanical application or products of PET nanocomposite

2 DEVELOPMENT

“Espacenet” and “Goldfire” databases were use to obtain the information of the patents. Different strategies have been used to do the search in the databases. Next tables present those strategies and the results obtained, it is also included the abstract of the patent and a brief evaluation according to the relationship and possible influence in the development of TECNA technical pilot project.

2.1 First search: Espacenet database, strategies:PET + nanocomposites+ glass fiber

PET + NANOCOMPOSITES + FIBER GLASS				
Publication number	Title/Applicant	Abstract	Year	Notes
CN101239725 (A)	Nano-stage calcium borate and use thereof JINGDEZHEN CERAMIC INST [CN]	The present invention provides a nanoscale calcium borate and its using purpose. The invention adopts adding boric acid, borax and calcium oxide in high pressure kettle according to mol ratio 32:1:4, the product is obtained by further adding 160-200ml distilled water to make pH of the reactant is 5-6, the compactness of the reaction kettle is between 0.50-0.75, moving the product to beaker after reacting 3-4 hours under the temperature 230-245 Celsius in a sealing condition, removing the upper clarifying solution after silencing by filling distilled water, washing again and again to make pH achieve neutral then drying. The width of single nanowires crystal is 90nm-110nm, the length is above 1 mum, the chemical formula is 2CaO.3B2O3.H2O. The nano-calcium borate may add in polymer system, used for inflaming retarding of rubber, nylon, plastic, paint, glass fibre reinforced plastic, coat, paper industry.	2008	Written in Chinese
EP1770115 (A1)	Fibre-reinforced sheet-like semi-finished product QUADRANT PLASTIC COMPOSITES AG [CH]	Method for preparing fiber-reinforced, thermoplastically pressable, flat semi-finished articles (A) by mixing a thermoplastic polymer (I) with reinforcing fibers (II) then hot pressing. The new feature is that (I) is a nanocomposite of 80-99wt.% polymer (Ia) and 1-20wt.% nanoparticles (NP). An independent claim is included for (A) that contain 99-80 parts (I); 1-20 parts NP and 20-800 parts (II). POLYMERS Preferred Articles: These contain 10-80wt.% nanocomposite (NC) and 90-20wt.% (II). Preparation: Hot pressing is done at a temperature above the softening point of (Ia). Particularly (a) NC is melted and combined, directly or after formation of a film, with flat (II)-containing mats, articles or fabrics, and hot pressed to (A); (b) NC is melted, combined, in an extruder, with an endless reinforcing fiber so that the fiber is broken and the product compressed to a strip of material; (c) NC is spun to form fibers, these cut and mixed with (II) of length 2-15 cm, then the mixed fiber fleece optionally needled and hot pressed; or (d) NC granules are milled to powder which is dispersed in water, the dispersion mixed with (II) of length 0.5-15 cm, then the mixture dried and hot pressed. Preferred Materials: Suitable reinforcing fibers are of glass, carbon, polyamide or relatively low m. pt. polyester. INORGANIC CHEMISTRY Preferred Material: NP are platelets of layered silicates (specifically MMT) with particle size 50-1500 nm and thickness 0.5-10 nm, particularly smaller than the diameter of (II).	2007	Written in German Different ways of incorporating glass fiber to nanocomposite: hot pressed, extruder with fiber, predispersion. Nanoparticles used:MMT

2.2 Second search: Espacenet database, strategies: PET + nanocomposite

PET + NANOCOMPOSITES				
Publication number	Title/Applicant	Abstract	Year	Notes
US2009117399 (A1)	Multilayer Nanocomposite / PACKAGING FILMS NEXT GENERATION FILMS INC [US]	The invention relates to multi-layer polymer nanocomposite packaging films having barrier properties. A co-extruded multi-layer packaging film includes a plurality of thermoplastic polymer layers, at least one polyamide layer and an adhesive blended into at least one of the thermoplastic polymer and polyamide layers.	2009	No related with TECNA project because final application is packaging films
US2009029167 (A1)	Polymer nanocomposites including dispersed nanoparticles and inorganic nanoplatelets TEXAS A & M UNIV SYS [US]; KANEKA CORP [JP]	The invention relates to the formation of polymer nanocomposites. A polymer nanocomposite comprises a polymer containing dispersed nanoparticles and nanoplatelets. The polymer nanocomposite may be formed by mixing a first composition of nanoparticles, a second composition of nanoplatelets and a third composition of a polymer material. Alternatively, for some polymeric materials, further processing steps to form the nanocomposite may be performed, such as precipitation and/or curing. The nanoparticles are selected from the group consisting of a metal oxide (oxide zinc, oxide titanium, and combinations thereof), an element particle and combinations thereof (silver, gold, and combination thereof)The inorganic nanoplatelets comprise a material having one or more elements selected from the group consisting of aluminium, zirconium, silicon, magnesium, titanium, hafnium, and combinations thereof. The polymer nanocomposite may be polyethylene terephthalate.	2009	Also published like: WO2009014685 (A1). Is not in relationship with PET material but with epoxy resins.
WO2009126670 (A1)	Bumper energy absorbers for pedestrian safety. DU PONT [US]; SILER MICHAL [CZ]; VAN DER LELIJ ADAM J [CH]	Bumpers are used on vehicles to absorb shock and impact from collisions and to thereby prevent or minimize injury to passengers and to curtail damage to the vehicle. In addition, bumper systems are government-regulated and must meet legislated. Specific dimensions and geometry of the bumper is the main objective of the patent where describe the mechanical characteristic of the material that can be used. There is no definition for material, it can be used any material, also nanocomposites which the correct mechanical properties.	2009	Also published like: US2007173585 (A 1) No definition of material , more related with geometry and design of the component.

PET + NANOCOMPOSITES				
Publication number	Title/Applicant	Abstract	Year	Notes
US2009039308 (A1)	Nanocomposite polymers	Modified polymers are prepared by providing a nanotube or nanoparticle suspension, adding a preformed polymer, swelling the preformed polymer in the suspension, and isolating the modified polymer from the suspension. The polymer may be a swellable polymer in the form of polymeric yarns, fibres, fabrics, ribbons or films. The swelling may be carried out using ultrasonic treatment.	2009	Also published like: WO2007010517 (A1) EP1910220 (A1). Pre-dispersion of nanoparticles in suspensions. Preparation of Kevlar nanocomposites
EP2070978 (A2)	Carbon nanotube-based composite material and method for fabricating same TSING HUA UNIVERSITY [CN]; HON HAI PREC IND CO LTD [TW]	A carbon nanotube-based composite material includes a polymer matrix and a plurality of carbon nanotubes in the polymer matrix. The plurality of carbon nanotubes forms a carbon nanotube film structure. A method for fabricating the carbon nanotube-based composite material includes: providing at least one carbon nanotube film, each including a plurality of carbon nanotubes; forming the carbon nanotube film structure and providing a polymer material of the polymer matrix; and filling the polymer material in the carbon nanotube structure to form the carbon nanotube-based composite material comprising the carbon nanotube film structure and the polymer material.	2009	Formation of CNT films and structures to be complete with polymer matrix, PET among others
US 2009104386 (A1)	Oriented nanofibers embedded in a polymer matrix	A method of forming a composite of embedded nanofibers in a polymer matrix is disclosed. The method includes incorporating nanofibers in a plastic matrix forming agglomerates, and uniformly distributing the nanofibers by exposing the agglomerates to hydrodynamic stresses. The hydrodynamic said stresses force the agglomerates to break apart. In combination or additionally elongational flow is used to achieve small diameters and alignment. A nanofiber reinforced polymer composite system is disclosed. The system includes a plurality of nanofibers that are embedded in polymer matrices in micron size fibers. A method for producing nanotube continuous fibers is disclosed. Nanofibers are fibrils with diameters 100 nm, multiwall nanotubes, single wall nanotubes and their various functionalized and derivatized forms. The method includes mixing a nanofiber in a polymer; and inducing an orientation of the nanofibers that enables the nanofibers to be used to enhance mechanical, thermal and electrical properties. Orientation is induced by high shear mixing and elongational flow, singly or in combination. The polymer may be removed from said nanofibers, leaving micron size fibers of aligned nanofibers.	2009	Also published like: US2006047052 (A1) Oriented nanofiber composite. Nanofiber fabrication and use in different polymers, PET among others.

PET + NANOCOMPOSITES				
Publication number	Title/Applicant	Abstract	Year	Notes
WO2008082495 (A1)	Polyester nanocomposites filaments and yarn DU PONT [US]; SEVENICH GREGORY JAMES [US]; WILLIAMSON DAVID T [US]	A method is provided herein for increasing modulus of polyester monofilament, comprising the steps: a. preparing a polyester nanocomposite by mixing a sepiolite-type clay with at least one polyester precursor selected from the group consisting of: (i) at least one diacid or diester and at least one diol; (ii) at least one polymerizable polyester monomer; (iii) at least one linear polyester oligomer, and (iv) at least one macrocyclic polyester oligomer; b. subsequently polymerizing the at least one polyester precursor in the presence or absence of solvent; and c. spinning monofilament comprising the polyester nanocomposite so produced; and d. optionally, preparing multifilament yarn comprising the monofilament so produced. Also provided are monofilament and multifilament yarn comprising a polyester nanocomposite into which is incorporated an effective amount of exfoliated sepiolite-type clay.	2008	Also published like: WO2008082495 (B1) US2007173585 (A 1) Preparation of monofilament of polyester, PET among others with sepiolite by means of in situ polymerisation.
US 2008207801 (A1)	Compatibilization of Polymer Clay Nanocomposites CANADA NAT RES COUNCIL [CA]	A polymer nanocomposite contains layered clay dispersed in a polymer matrix together with compatibilizers for the clay and polymer matrix. The compatibilizers are a combination of two or more graft polymers. One graft polymer has high functionality and short chain length and another graft polymer has low functionality and long chain length. Such polymer nanocomposites have improved dispersion and better strength and modulus, while maintaining good toughness and impact strength. The polymer nanocomposites are particularly useful in applications where good mechanical performance and light-weight are of importance.	2008	Also published like: WO2006066390 (A1) KR20070092743 (A) JP2008525536 (T) EP1831302 (A1) EP1831302 (A4) Relates to polymer/clay nanocomposites and to methods for modulating polymer-clay interactions in nanocomposites. Used of graft polymers and different polymers like matrix.

PET + NANOCOMPOSITES				
Publication number	Title/Applicant	Abstract	Year	Notes
WO200810033 (A2)	Polymer composites mechanically reinforced with alkyl and urea functionalised nanotubes. UNIV RICE WILLIAM M [US]; KHABASHESKU VALERY N [US]; PULIKKATHARA MERLYN X [US]	A polymer composite includes a polymer matrix and an alkyl-substituted carbon nanotube. A polymer composite also includes a polymer matrix and a fluorinated carbon nanotube reacted with urea, thiourea, or guanidine. A method of functionalizing a carbon nanotube includes heating a fluorinated carbon nanotube with urea, thiourea, or guanidine. A substituted carbon nanotube includes a fluorinated carbon nanotube and amino silane compounds. The amino silane compounds covalently link to the fluorinated nanotube through the amino functional group. Polymer composites, ceramics and surface coating materials may be constructed from these substituted carbon nanotubes.	2008	Also published like: WO2008100333 (A3) Polymer matrix with alkyl-substituted carbon nanotube or fluorinated carbon nanotube. Different thermoplastic matrix, PET among others and also thermosets matrix.
WO2008156891 (A2)	Improvements in nanocomposites and their surfaces UNIV POLYTECHNIC [US]; LEWIN MENACHEM [IL]; TANG YONG [CN]	A method for preparing nanocomposites and nanocomposite polymeric products by dispersing nanoparticles in a polymer either by melt processing or by solution processing and bringing about migration of the nanoparticles from the bulk interior to the surface of the nanocomposites. These surfaces impart highly enhanced properties to the nanocomposites as compared to the pristine polymer and to nanocomposites that have not undergone the migration process, including stability against aging, longer shelf life, higher hydrophobicity, higher wear resistance, higher hardness and lower friction.	2008	Also published like: WO2008156891 (A3) Melt mixing of nanoparticles and polymer in oxidations conditions to create polarity in polymer to obtain better exfoliation and dispersion.
US2008242785 (A1)	TiO ₂ -coated CNT, TiO ₂ -coated CNT reinforced polymer composite and methods of preparation thereof UNIV TSINGHUA [TW]	A method of preparing carbon nanotube/polymer composite is disclosed, which includes: forming a layer of TiO ₂ on carbon nanotubes (CNTs) with a precursor of TiO ₂ by a sol-gel or hydrothermal method, a weight ratio of the TiO ₂ precursor to CNT being 0.3:1 to 30:1; modifying the TiO ₂ -coated CNTs with a coupling agent to improve the affinity thereof to a polymer; and mixing a polymer with the resulting modified TiO ₂ -coated CNTs to form a TiO ₂ -coated CNT reinforced polymer composite. The mechanical properties of the polymer composite can be enhanced by using an additional fiber reinforcement material.	2008	TiO ₂ -coated CNT-reinforced polymer. PET matrix among others, including thermosets.

PET + NANOCOMPOSITES				
Publication number	Title/Applicant	Abstract	Year	Notes
EP1810993 (A2)	Method of preparation of polyethylene terephthalate nanocomposite fiber with enhanced modulus HYOSUNG CORP [KR]	The present invention relates to a polyethylene terephthalate nanocomposite fiber with enhanced modulus, and specifically to a technique for preparing a PET nanocomposite fiber with excellent initial and high-temperature modulus, which comprises adding 1 to 4% by weight of a compound selected from the group consisting of C ₅₆ H ₁₂₂ O ₁₂ Si ₇ , C ₃₁ H ₇₁ NO ₁₂ Si _{8n} , C ₅₉ H ₁₂₇ NO ₁₂ Si ₈ , and C ₃₃ H ₇₆ N ₂ O ₁₂ Si ₈ , each of which is an organic/inorganic hybrid nanocompound, based on the total weight of the polymers, to prepare a polyethylene terephthalate nanocomposite chip having 85 mol% or more of the ethylene terephthalate units and an intrinsic viscosity in the range of 0.50 to 1.20, and then melt-spinning and stretching the composite chip.	2007	Also published like: EP1810993 (A3) JP2007182665 (A) US2007155878 (A1) PET nanoreinforced used like a synthetic fiber. Nanoclays, POSS
WO2006069128 (A1)	Compositions of polyesters and sepiolite type clays DU PONT [US]; WILLIAMSON DAVID T [US]	Compositions of thermoplastic polyesters and sepiolite-type clay in which the clay is dispersed in the polyester as often fibrous particles whose smallest dimension is less than 100 nm are made by polymerizing the polyester precursors in the presence of the clay. The compositions have good physical properties and can be melt moulded into various articles. Many of these articles may be coated (painted) and are especially useful for appearance parts such as visible exterior automotive body parts.	2006	Also published like : WO2006069128 (A8) WO2006086080 (A1) US2008261062 (A1) US2009192254 (A1) US2006205856 (A1) In situ polymerisation of PET and Cloisite 25A..
EP2006323 (A1)	Process for the production of polyester nanocomposites DU PONT [US]	A method for dispersing sepiolite-type clay particles in a polyester matrix by melt-compounding a mixture of: sepiolite-type clay, at least one linear polyester oligomer, and at least one polyester polymer to produce a nanocomposite composition; and, optionally, subjecting said nanocomposite composition to solid state polymerization to increase polyester molecular weight. Further described is a method for preparing a polyester nanocomposite composition from a masterbatch, comprising melt-compounding a mixture of: sepiolite-type clay, at least one polyester oligomer, and at least one polyester polymer to produce a nanocomposite composition containing a greater concentration of sepiolite-type clay than is desired in the final resin composition; optionally, subjecting said nanocomposite composition to solid state polymerization to increase the polyester molecular weight; and further melt compounding said nanocomposite composition with polyester polymer and, optionally, additional ingredients.	2006	Also published like: US2008315453 (A1) KR20080112980 (A) JP2009001796 (A) CA2634793 (A1) In situ polymerisation of PET and sepiolite.

PET + NANOCOMPOSITES				
Publication number	Title/Applicant	Abstract	Year	Notes
MXPA03010800 (A)	Method for obtaining nanocomposite films and laminates from thermoplastics and clays UNIV MEXICO NACIONAL AUTONOMA [MX]	The present invention refers to a method for obtaining nanocomposite films and laminates from thermoplastics and clays useful as roofs, placards, panels, partition frames and in stamping and thermoforming processes. The clays used for the aforesaid method are: sodium clay, calcium clay, sodium montmorillonite, calcium montmorillonite, vermiculite, synthetic clays, smectic clays, beidellites, nontronites, and mixtures thereof. The clays are chemically modified with maleic anhydride and pentaerythritol. The thermoplastics used for said method are: low and high-density polyethylenes, lineal polyethylenes, and high and ultra high molecular weight polyethylenes, acetals, polypropylene, polyvinyl chloride, polystyrene, polyethylene terephthalate and polybutylene terephthalate. The manufacture of said nanocomposites includes two steps: the first step consists in manufacturing a nanocomposite of the granule-type by means of simultaneously extruding the polymer and the clays in a two spindle extruder. In the second step the granules are processed in a single spindle extruder, where the product is provided with the desired shape. The nanocomposites obtained by said method present improvements in tension mechanical properties in comparison with the virgin polymer.	2005	Fabrication of roofs, placards, panels using modified nanoclay with polymer in a double twin screw.
US2003134942 (A1)	Method for producing a well-exfoliated and dispersed polymer silicate nanocomposite by ultrasonication LEE ELLEN CHENG-CHI, ; MIELEWSKI DEBORAH FRANCES, ; FORD GLOBAL TECHNOLOGIES, LLC	The present invention discloses a method for dispersing and exfoliating fillers in a thermoplastic polymer by sonicating a mixture of the thermoplastic polymer and the filler. The method of the present invention is particularly useful in dispersing layered silicate clays in thermoplastic polymers. A reinforced composite comprising a filler dispersed in a thermoplastic polymer is also disclosed. In another variation, the method of the invention is incorporated into conventional plastic extruder and injection molding equipment.	2004	Also published like: US6828371 (B2) US2005122834 (A1) Dispersion of nanoclays by means of sonication while the polymer is in a melted state. Aluminium silicate clays amount others.

PET + NANOCOMPOSITES				
Publication number	Title/Applicant	Abstract	Year	Notes
US6458879 (B1)	Thermoplastic materials containing nanocomposites and an additional elastomer BASF AG [DE]	<p>The invention relates to thermoplastic nanocomposites, comprising. a) a thermoplastic (A), b) at least one compound (B) (delaminated phyllosilicate), whose structure has been built up from negatively charged phyllosilicates and from cations embedded between these, and which have been dispersed uniformly in component (A), and (c) a rubber or rubber mixtures (C), where component (C) has a particle size distribution with a d(50) value of from 10 to 1000 nm. The invention further relates to a process for preparing these nanocomposites, and also to their use.</p> <p>The thermoplastics have preferably been selected from the group consisting of polyamides, vinyl polymers, polyesters, polycarbonates, polyaldehydes and polyketones.</p> <p>Polyesters are also suitable thermoplastics, preferably those based on terephthalic acid and diols, particularly preferably polyethylene terephthalate and polybutylene terephthalate.</p>	2002	<p>Also published like: DE19854170 (A1) PL347974 (A1) JP2002530506 (T) EP1133530 (A1) EP1133530 (B1)</p> <p>Use of thermoplastic, rubber and delaminated phyllosilicate. Use of PET amount other polymers. Preparation by in situ polymerisation, melt intercalation</p>

2.3 Third search: Goldfire database, strategies:PET + nanocomposite

PET + NANOCOMPOSITES				
Publication number	Title/Applicant	Abstract	Year	Notes
US2009089941 (A1)	Process for Creating Composite Materials to Produce Polymer Nanocomposite Films that Exhibit Improved Light Fastness Properties UNIV SOUTH CAROLINA [US]	The present invention relates to new methods of producing polymer composite materials. More specifically, the invention involves a process in which layered materials including clays and other inorganic materials are dispersed into polymer systems to create polymer nanocomposite films. The resulting films exhibit improved resistance to fading when compared to polymer films that lack the additional layered materials.	2009	Also published like: WO2006110628 (A2) WO2006110628 (A3) Nanoparticles of synthetic oxide particles. Development of colored polymeric material having increased light fastness. Predispersion with sonication and in situ polymerisation
US2009064425 (A1)	Polymer/Clay Nanocomposite Films with Improved Light Fastness Properties and Process for Producing Same UNIV SOUTH CAROLINA [US]	A colored polymeric material having improved light fastness is generally provided. The colored polymeric material generally comprises a polymer, a colorant, and natural nanoparticles. The colorant can be a dye, such as an acid dye. In one embodiment, the dye can be susceptible to degradation when exposed to light in the presence of oxygen, such as many azo dyes. The natural nanoparticles can include many natural clays.	2009	Also published like: WO2006110627 (A1) Clay nanoparticles, Predispersion with sonication and in situ polymerisation
US2009186179 (A1)	Polyester clay nanocomposites for barrier applications DU PONT [US]	The present invention is a method for reducing the permeability of gases through polyester containers and films by incorporating into the polymer from which the container or film is formed an effective amount of exfoliated sepiolite-type clay.	2009	Also published like: WO2006069131 (A1) US2006141183 (A1) JP2008525595 (T) EP1838756 (A1) EP1838756 (B1) Films and barrier properties. In situ polymerisation

PET + NANOCOMPOSITES				
Publication number	Title/Applicant	Abstract	Year	Notes
US6841211 (B1)	Containers having improved barrier and mechanical properties PECHINEY EMBALLAGE FLEXIBLE EU [US]	The present invention relates to containers for flowable products having improved barrier and/or mechanical properties and methods for making said containers. These improvements are achieved by incorporating into at least one layer of the container structures a polymeric nanocomposite comprising a polymer and nanosize particles of a modified clay.	2005	Also published like: WO0187580 (A1) EP1286825 (A1) CA2408741 (A1) CA2408741 (C) AU6304101 (A) AR029923 (A1) Not in relationship with TECNA project, use of nanocomposites in containers.
US20042599 99 (A1)	Polyester/clay nanocomposite and preparation method KOREA INST SCIENCE TECHNOLOGY [KR]	Disclosed are a polyester/clay nanocomposite, and a preparation method thereof, comprising mixing a cyclic ester oligomer with a layered clay having an enhanced hydrophobicity and directly polymerizing the cyclic ester oligomer. The polyester/clay nanocomposite has an excellent processibility due to its low melting viscosity and has excellent mechanical and electrical properties. Therefore, it can replace conventional polyester resin applied as electronic material, as well as can be used as a compatibilizing agent for increasing compatibility of the conventional polyester/clay composite.	2004	Also published like: KR20040110891 (A) Prepared from a cyclic oligomer and nanoclays organically modified
US20041276 27 (A1)	Polymer/clay nanocomposite comprising a clay treated with a mixture of two or more onium salts and a process for making same GILMER JOHN WALKER, ; BARBEE ROBERT BOYD, ; MATAYABAS JAMES CHRISTOPHER	This invention relates to a polymer-clay nanocomposite comprising (i) a melt-processible matrix polymer, and incorporated therein (ii) a clay-organic cation intercalate comprising a layered clay material intercalated with at least two organic cations, wherein at least one organic cation comprises ligands each having 7 or less carbons and at least one organic cation comprises at least one ligand having 12 or more carbons. The invention also relates to a process for preparing a nanocomposite and articles produced from a nanocomposite.	2004	Polymer clay nanocomposite having improved gas permeability. Clay material intercalated with a mixture of organic cations. Preparation by metl compounding

PET + NANOCOMPOSITES				
Publication number	Title/Applicant	Abstract	Year	Notes
US2004063841 (A1)	Process for preparing an exfoliated, high I. V. polymer nanocomposite with an oligomer resin precursor and an article produced therefrom GILMER JOHN WALKER, ; MATAYABAS JAMES CHRISTOPHER, ; CONNELL GARY WAYNE, ; OWENS JEFFREY TODD, ; TURNER SAM RICHARD, ; PINER RODNEY LAYNE	This invention is directed to a process for preparing an exfoliated, high I.V. polymer-platelet particle nanocomposite comprising the steps of: (i) melt mixing platelet particles with a matrix polymer-compatible oligomeric resin to form an oligomeric resin-platelet particle composite, and (ii) mixing the oligomeric resin-platelet particle composite with a high molecular weight matrix polymer, thereby increasing the molecular weight of the oligomeric resin-platelet particle composite and producing an exfoliated, high I.V. polymer nanocomposite material. The invention also is directed to a nanocomposite material produced by the process, products produced from the nanocomposite material, and a nanocomposite prepared from an oligomeric resin-platelet particle precursor composite.	2004	Clay nanoparticles predispersed in an polymer-compatible oligomeric resin and then into the matrix polymer. Gas barrier properties
US2003149154 (A1)	Method for producing nanoreinforced thermoplastic polymers HEINEMANN KLAUS, ; TAEGER EBERHARD, ; MEUSEL ERICH, ; MUELLER WOLFGANG	This invention relates to the use of organophilic, swellable specially modified phyllosilicates in the production of nano-reinforced thermoplastic polymers, preferably polyamides, polyesters and polycarbonates. The inorganic phyllosilicate particles are bonded to or incorporated into the polymer in a covalent manner with nanodistribution. Special modification enables the phyllosilicates to be used as initiators in the case of polymerization or a chain elements in the case of condensation. The covalent bonding of the phyllosilicate particles to the polymer increases the stability of the reinforcing effect as opposed to an ionic bond. The special modification is performed for phyllosilicates which become hydrophobic as a result of cationic exchange. This property makes it possible for certain organic reaction partners to reach reactive groups present on the surface of the phyllosilicate and to react therewith on certain conditions. As a result of the functional groups containing organically modified phyllosilicates arising from the reaction, they are able to form stable, covalent bonds with the polymers.	2003	Also published like: WO0196459 (A1) JP2004503642 (T) EP1299467 (A1) DE10128356 (A1) CN1436205 (A) AU7626801 (A) In situ polymerisation with modified sheet silicate (MMT, hectorite, illite...)

PET + NANOCOMPOSITES				
Publication number	Title/Applicant	Abstract	Year	Notes
US6486254 (B1)	Colorant composition, a polymer nanocomposite comprising the colorant composition and articles produced therefrom UNIV SOUTH CAROLINA RES FOUNDA [US]	This invention relates to a colorant composition comprising a layered clay material intercalated with at least one cationic colorant, optical brightener or a mixture thereof. This invention also relates to a polymer-clay nanocomposite comprising (i) a melt-processible matrix polymer, and (ii) a layered clay material intercalated with at least one cationic colorant, optical brightener or a mixture thereof, wherein the clay-cation colorant/optical brightener intercalate is incorporated into the matrix polymer. The invention further relates to articles produced from the polymer nanocomposite.	2002	In situ polymerisation and met mixing. Modified clay nanoparticles
US6084019 (A)	High I.V. polyester compositions containing platelet particles EASTMAN CHEMICAL CORP [US]	The present invention relates to polyester-platelet particle composite compositions comprising about 0.01 to about 25 weight percent platelet particles dispersed in at least one polyester wherein said composition has an I.V. of greater than about 0.55 dl/g, low shear melt viscosity greater than about 30,000 poise and a gas permeability which is at least 10% lower than that of unmodified polyester and processes for producing same.	2000	Also published like: WO9829499 (A1) JP2001507743 (T) EP0950077 (A1) EP0950077 (B1) CA2276393 (A1) BR9713799 (A) AT275167 (T) Used in moulded objects, bottles, food containers. Nanoparticles use: MMT, bentonite, saponite... In situ polimerization

3 CONCLUSIONS

- Two patents of hybrid material of PET-GF-nanoparticles as is going to be used in TECNA patents have been found. Patent “EP1770115” shows the different ways of incorporating glass fiber to nanocomposite: hot pressed, extruder with fiber, predispersion.
- Nanoclays, and in some cases modified nanoclays are the most commonly used to prepare nanocomposites of PET matrix. Others nanoparticles used are CNT, sepiolite and POSS.
- Most of the patents present the “in situ polymerisation” as the way of obtained well dispersed nanocomposites.
- The majority of the patents are for packing products or films.

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Zaragoza, 18^h January 2010

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