Improvement of properties of polymeric matrices by realizing hybrids and nanocomposites: perspectives in the transport sector.

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Drivers for materials development in automotive and aerospace industry

Main driver behind materials innovation in the automotive / aeronautics industry is to decrease energy consumption via reducing the weight of the structural parts.

In addition to the energy savings, the objective is to improve stiffness, strength and reliability along with manufacturing speed, enhancing environmental and thermal stability, and promoting recycling.
Drivers for materials development in automotive and aerospace industry

The aeronautics business remains extremely conservative and risk averse, making it difficult for new applications to be integrated in new products. Main goals are:

- increased safety
- reduced emissions
- reduced noise
- increased capacity
- increased range
- enhanced payload
- higher speed
- lower operating and maintenance costs
- better overall management of the aircraft and its use

Most important for reaching these objectives is the development of a new generation lighter materials.
**NANOCOMPOSITES**

*Nanocomposite: Composite* in which at least one of the phases has at least one dimension of the order of nanometer.

Advantage of using the nanocomposites:

- Greater tensile and flexural strength for the same dimension of plastic part
- Impact and damage tolerance
- Reduced weight for the same performance
- Increased dimensional stability
- Improved gas barrier properties for the same film thickness
- Flame retardant properties
- Improved mechanical strength
- Higher electrical conductivity
- Higher chemical resistance
- Good thermal properties (high T resistance, thermal shielding)
- Thermal conductivity
- Electric and magnetic properties (EMI shielding)
- Fire retardancy
- Wear/friction and scratch resistance

VALUE OF WORLD MARKET OF NANOCOMPOSITES in 2009 = 1 billion euros and 500,000 tons (80% thermoplastic matrices and 20% thermoset matrices)
POLYMER NANOCOMPOSITES

Introducing small amounts of Nanoparticles in a polymer matrix we obtain:

– Dramatic changes in Mechanical, Thermal, Physical, Electrical and / or Chemical Properties

– Multifunctionality
  (Structural + Electric; Structural + ElectroMechanical; Structural + Permeability; Structural + Biocompatibility)

– Minimal change in density of the polymer

– Possibly Inexpensive enhancement of polymer matrix properties

  Challenges

– Dispersion (Equilibrium; Kinetics; Processing)

– Alignment

– Interface Control

– Optimization & Pricing

– Processing
POLYMER NANOCOMPOSITES

Types of reinforcements:
1D: carbon nanotubes (CNT), carbon nanofibers (CNF)
2D: nanoclays, graphene
3D: nanoparticles
Types of reinforcements: interpenetrated polymer-silica hybrid

Poly (amic acid) in NMP

Polymer Nanocomposites

TEOS

GOTMS
NANOCOMPOSITES: PMDA-ODA/Silica hybrid

Microcomposite (MC)

Nanocomposite (NC)
POLYMER NANOCOMPOSITES
Mechanical properties

E. MANIAS, G. POLIZOS, H. NAKAJIMA, AND M. J. HEIDECKER, 2007

POLYMER NANOCOMPOSITES
Thermal and barrier properties

E. MANIAS, G. POLIZOS, H. NAKAJIMA, AND M. J. HEIDECKER, 2007
POLYMER NANOCOMPOSITES
Processability

After G. Camino, M. Lavaselli, A. Frache et al., 2010
POLYMER NANOCOMPOSITES

Opportunities:
- Interface to volume ratio
- Unique nanoparticle properties
- Heterogeneity less than 'critical flaw size')
- Emergent behavior: associative network of elements

Vaia, Materials Today, 2006;
Chemistry of Materials, 2007;
Science (Perspective), 2008
Polymers nanocomposites

Nanofoams

PS foam
Cell size: 20µm
Cell density: $8.23 \times 10^7$ cells/cm$^3$

PS/1wt%CNF foam
Cell size: 2.64µm
Cell density: $2.78 \times 10^{10}$ cells/cm$^3$

Nanofillers serve both as a nucleating site to raise cell density promoting formation of microcellular foams and as a reinforcing agent. Potential commercial markets for ultra-low density nanocomposite foams and sandwich structures may include electronic housing for satellites and telecommunication systems; electronic housing and structural components for commercial aircraft, boats, ships, trains, buses, trucks, automobiles; and shipping containers, building panels, and many others.
POLYMER NANOCOMPOSITES
3-phase composite

Kuang-Ting Hsiao, 2004
One of the expected advantages of nanocomposites as matrix polymer is an **increase in compressive strength** of the fibre composite because of the higher matrix modulus. Also **flexural strength** of the fibre composite is increased due to the much higher matrix modulus. This could especially be favourable for moisture sensitive polymers like nyons, which loose a lot of their stiffness in moist conditions. **Interlaminar strength, toughness** and **fiber/matrix adhesion** increase as well.
About 100% improvement in the delamination performance when 1wt% of CNF were dispersed into a polyester resin matrix and infused into the glass fiber preform as also proven by comparing the fracture surfaces of the hybrid composite and the conventional composite specimens after delamination tests and the comparison in G_IC values.
APPLICATIONS OF POLYMER NANOCOMPOSITES
POLYMER NANOCOMPOSITES
Automotive applications

Basell commercial Automotive nanocomposites

Partnering Relationships-General Motors & Basell & Southern Clay

- Commercial applications
- M-Van Step Assist, 08/01
- Impala side moldings, 02/04
- Hummer H2 SUT trim, panels (05/04)
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Automotive applications

Stone Impact Stress Whitening: customer data

- Property related to scratch resistance

Conventional  Nanocomposite
POLYMER NANOCOMPOSITES
Automotive applications

Paint Adhesion: customer data

Conventional  Nanocomposite
POLYMER NANOCOMPOSITES
Automotive applications

Engine covers (dimensional stability, thermal resistance, superior surface finishing, weight reduction)

CNT nanocomposites for fuel systems: tanks, fittings, tubing pumps/filters (antistatic properties, improved barrier, higher impact resistance)

Interior parts
POLYMER NANOCOMPOSITES
Automotive applications

Possible solutions through nanomaterials

- Economical **lightweight** parts that enhance fuel efficiency and vehicle durability. The advantage of using a nanocomposite for automotive applications is **that less filler material** is required to provide the **same or better performance characteristics** when compared to conventional materials, **transparency**, less **permeability** and increased **strength** (clay nanoparticles), **safety** for example flame-retardant materials.

- The **fire retardancy** properties demonstrated by nanocomposites promise to create a whole new class of polymers for use in the **interior** of the automobile. The weatherability of nanoplatelet-reinforced composites offer extended useful life for exterior components.

- **Green nanocomposites**, based on carbohydrate chemistry, promise to provide a new definition for recyclability and bio-decomposition.

- Possibility to realize parts that can be **electrostatically painted**.
Advantages of nanomaterials relevant in aeronautical applications are:

- ultra high **strength to weight ratio**
- improved **hardness, wear resistance** and **resilience**
- **thermal shock, fatigue** and **creep** resistance
- **multi-functional materials** can reduce weight by reducing the number of components

Nanomaterials can enhance the properties of almost every material used in aircraft building.
POLYMER NANOCOMPOSITES
Aeronautical applications (perspective)

The airframe is the main target for the use of nanomaterials, aiming at a weight reduction and therefore decreased fuel consumption and costs because of the strength of nanomaterials.

Nanocomposite properties can also be exploited by tailoring of mechanical properties (e.g. property gradient materials) or by realizing self-healing materials.

Thermal stability and enhanced fire retardancy through char formation have motivated investigation of PCNs as a component to anti-flammability additives for aircraft interiors.

Polymers obtained by additivation of carbon nanofiber have different aerospace applications like aircraft engine anti-icing, fire retardant coatings (forming a char layer over combustible composites), lightning strike protection, conductive aerospace adhesives, thermo-oxidative resistant structures, missile/airframe structures. The electrical conductivity can also be used to realize wires.
Potentially very interesting materials are composite materials reinforced with carbon nanotubes. **Carbon Nanotube reinforced polymers** are investigated for aerospace applications because of their **good strength to weight ratio, flame and vibration resistance, antistatic and electrical properties**.

High strength and lightweight composite laminates (incorporating carbon nanotubes in a variety of resins) are being investigated for use in **ballistic protection** and novel damping materials.

The feasible **reduction of the weight** of aircraft components using CNT can be as large as 60-70% compared to existing carbon fibre reinforced polymers. The **major hurdles** are the **10,000-fold increase in price** compared to standard fibres and the **lack of an appropriate industrial-scale production method**. Technical problems include a **lack of methods to achieve spatial alignment of CNTs**, good **adhesion to the polymer matrix** and achieving a **high loading rate**.
POLYMER NANOCOMPOSITES
Aerospace applications (perspective)

Due to their high mechanical strength and resistance against heat and radiation, nanoparticle reinforced polymers, have potential applications in various components in space as lightweight structural materials, housings of solid-propellant rockets, as heat protection material, electrical isolations or fire protection applications.

There is a huge potential for mass savings (CNT) in space structures, which represents one of the main goal of futures spacecraft. Another further advantage of carbon nanotubes based materials is the possibility of creating monitored materials.

This CNT nanoreinforced fiber composite can improve the resin-dominated properties such as shear strength of carbon fibre polycyanurate composites used in space hardware for stiff, lightweight structures.
Many aerospace applications require electrically conducting polymer based composites for static discharge, electrical bonding, EM interference shielding and current return through the structure. Improvement of electrical conductivity of composite laminates primarily in order to fulfil the requirements for lightning strike protection but also for electrical grounding,
CONCLUDING REMARKS

Nanocomposites bear high promise for enabling new uses and applications of polymer materials. In the simplest approach, they can expand the window of applications of a given polymer, and in the best case they can enable the use of polymer–matrix composites in applications where metal or ceramic materials are currently used.

One of the challenges is to move toward the development of methods to create well-defined three-dimensional morphologies of nanofillers: morphologies that contain highly aligned fillers, house-of-cards structures, edge-connected (starlike) formations, and alternating two- and one-dimensional fillers.
CONCLUDING REMARKS

The highest benefit of the hybrid character of nanocomposites comes from overcoming the property trade-offs associated with conventional composites: For example, nanocomposites can improve stiffness without sacrificing toughness, can enhance barrier properties without sacrificing transparency, can bestow flame retardancy without sacrificing mechanical properties, and can enhance mechanical performance and biodegradability simultaneously.

When such behaviors are enhanced synergistically with effects from other additives or fillers, they can effectively push the envelope of the current state of the art. Such approaches will develop particularly exciting systems where synergistic combinations of multiple nano- and macrofillers are properly combined in a multifiller composite material.