DEPARTMENT OF PHYSICS AND NANOTECHNOLOGY
SRM INSTITUTE OF SCIENCE AND TECHNOLOGY

Applications of Nanotechnology
Food Packaging and Food Safety

Overview

1. Introduction
2. History
3. Applications
4. Polymer Nanocomposites
5. Nano-coatings
6. Surface biocides
7. Active packaging
8. Intelligent Packaging
9. Nano sensors
10. Bio-plastics
11. Safety issues

Introduction

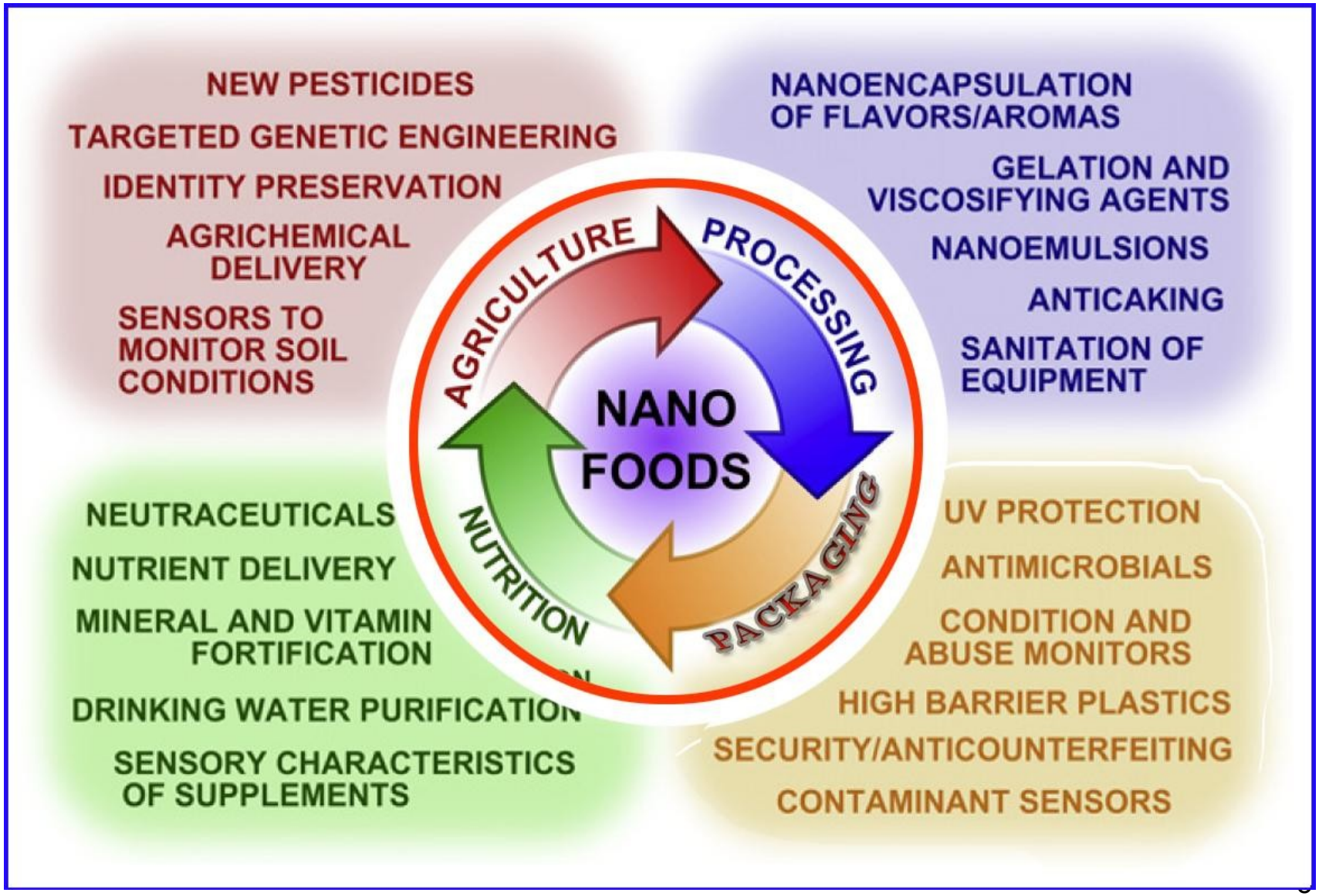
Packaging

Scientific method of enclosing food material/goods in a container and it ensure the delivery of goods to the ultimate consumer in the best condition indented for their use.

(Robertson, G. L., 2005)

Functions of Packagin

- Containment
- Protection
- Convenient
- Communication


NEW PESTICIDES
TARGETED GENETIC ENGINEERING
IDENTITY PRESERVATION
AGRICHEMICAL DELIVERY
SENSORS TO MONITOR SOIL CONDITIONS
NANOENCAPSULATION OF FLAVORS/AROMAS
GELATION AND VISCOSIFYING AGENTS
NANOEMULSIONS
ANTICAKING
SANITATION OF EQUIPMENT
AGRICULTURE
PROCESSING
NANO FOODS
NUTRITION
PACKAGING
NEUTRACEUTICALS
NUTRIENT DELIVERY
MINERAL AND VITAMIN FORTIFICATION
DRINKING WATER PURIFICATION
SENSORY CHARACTERISTICS OF SUPPLEMENTS
UV PROTECTION
ANTIMICROBIALS
CONDITION AND ABUSE MONITORS
HIGH BARRIER PLASTICS
SECURITY/ANTICOUNTERFEITING
CONTAMINANT SENSORS

MATERIALS	PROCESSING	PRODUCT	PRODUCT SAFETY
Nanoparticles	Heat/Mass Transfer	Controlled Delivery	Nanosensors
Nano-emulsions	Reaction Engineering	Formulation	Nanotracers
Nanocomposites	Biotechnology	Packaging	
Nanostructured Materials	Molecular Synthesis		

Basic Materials

Food Safety

Most attractive area of food Nano-science research and development is- **PACKAGING**

2008	2014
$ 4.13 billion	$ 7.3 billion

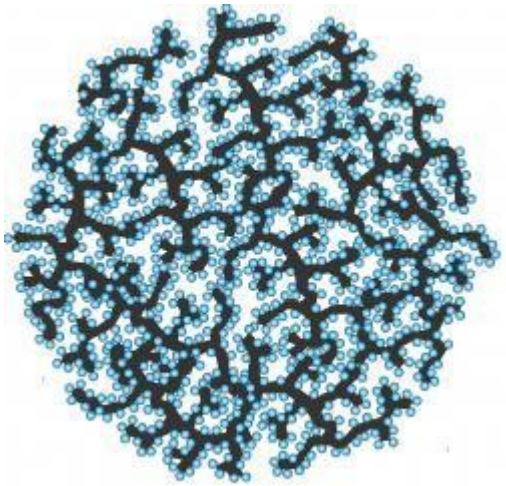
Annual growth rate 11.65%

www.innoresearch.net

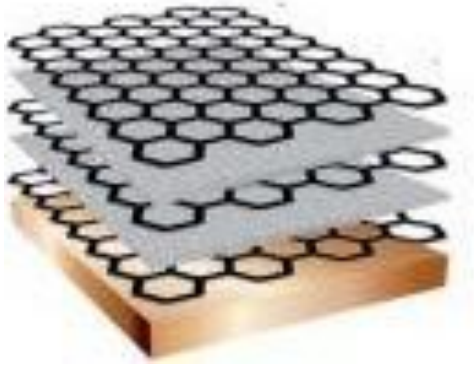
Application of Nano-materials in **Packaging**

Nano-materials

1. Polymer Nanocomposites
2. Nano-coatings
3. Surface biocides
4. Active
5. Intelligent Packaging
6. Bio-plastics



Silicon-carbon-nanocomposite



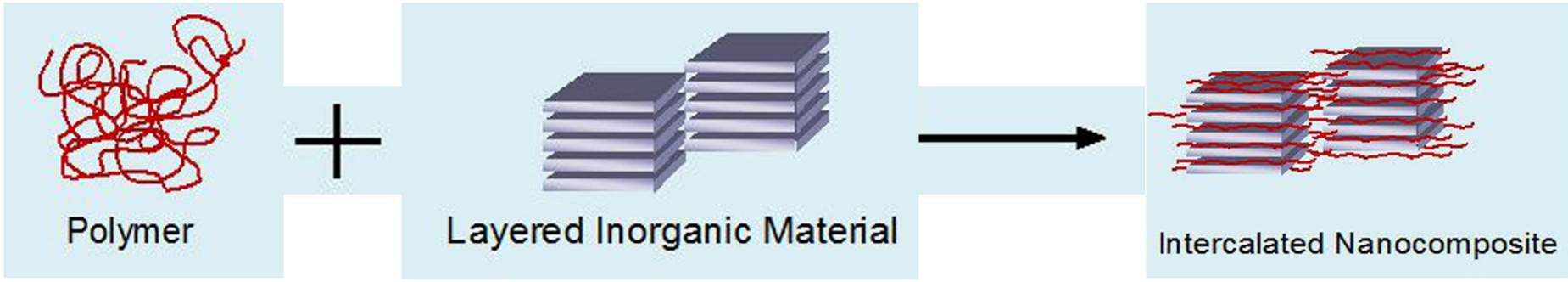
(Bradley, E.L. 2011)

1. Polymer Nano-composites

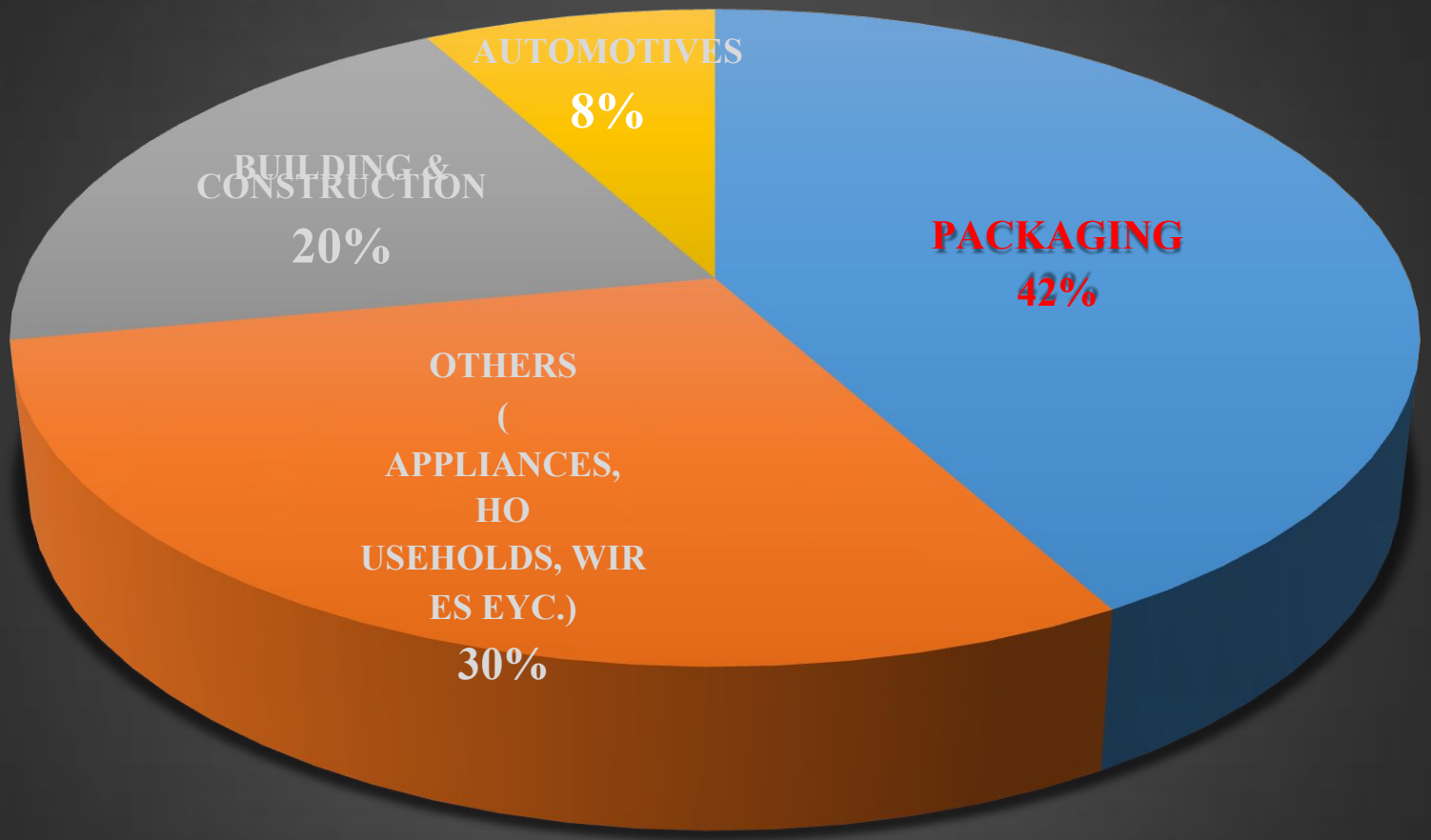
Incorporating nanomaterials into the packaging polymer to improve physical performance, durability, barrier properties, and biodegradation.

(Bradley, E.L. 2011)

Polymer Matrix + Nanomaterials= PNCs



POLYMER GLOBAL MARKET



Silvestre et al. (2011)

Polymer used in food packaging

1. **Polyolefins**
   - **Polypropylene(PP)**
   - **Polyethylene (HDPE, LDPE, etc.),**
2. **Polyethylene terephthalate (PET),**
3. **Polystyrene (PS)**
4. **Polyvinyl chloride (PVC)**
5. **Polyvinyldiene Choloride (PVdC)**
6. **Polycarbonates (PC)**
7. **Polyamides (nylons)**

……

- ✔ Strength and stiffness,
- ✔ Barrier to oxygen and Moisture
- ✔ Resistance to food component attack
- ✔ Flexibility.

……

Critical Issue

Migration

Permeability

OTR & WVTR

Plasticizers Ranked by Migration Effects on Plastics in Contact with PVC

ABS	Polycarbonate	Polystyrene	Acrylic
TOTM	Polymeric	Polymeric	Polymeric
DPHP	TOTM	TOTM	TOTM
DOTP	*DPHP*	DOTP	*DPHP*
DEHP	*DINP*	*DINP*	DINCH
DINCH	DINCH	*DPHP*	*DINP*
DINP	DOTP	*DEHP*	DOTP
Polymeric	*DEHP*	DINCH	*DEHP*
DOA	ATBC	DOA	DOA
ATBC	DOA	ATBC	ATBC
Benzoate	Benzoate	Benzoate	Benzoate

Plasticizers in red are not recommended for contact with the non-PVC material. Those in *italics* are phthalates. [Source: Teknor Apex Company]

Bisphenol A

DEHA: diethylhexyl adipate

- PET, provides a good barrier to oxygen (**O_2 permeability = 6-8 nmol/ m^1 s^1 GPa^1**), but highly permeable for water vapour

- Density polyethylene (HDPE) fares much worse (**O_2 permeability = 200-400 nmol/ m^1 s^1 GPa^1**) But HDPE offers a significantly better barrier against water vapor than PET.

- In some applications, high barriers to migration or gas diffusion are undesirable

(Eg:-fresh fruits and vegetables)

- High oxygen and carbon dioxide barriers is necessary

(Eg:-Plastics utilized for carbonated beverage containers)

(Finnigan et al., 2009)

(Finnigan et al., 2009)

Polymer nanocomposites (PNCs)

PNCs are created by dispersing an inert, Nano scale filler throughout a polymeric matrix.

Filler are

1. Clay and silicate nanoplatelets,
   (Duncan, T. V 2011)
2. Silica (SiO_2) nanoparticles,
   (Wu, C.L. et al. 2002)
3. Carbon nanotubes
   (Zhou, X. et al. 2007)
4. Graphene
5. Starch nanocrystals
   - (Chen, Y. et al. 2008)
6. Cellulose-based Nanofibers or
   - nanowhiskers
   - (Azeredo, H.M.C et al. 2010)
7. chitin or chitosan nanoparticles.
   - (Lu, Y. et al. 2004)
8. Other inorganics.
   - (Yang. Y et al 2008)

Properties of PNCs

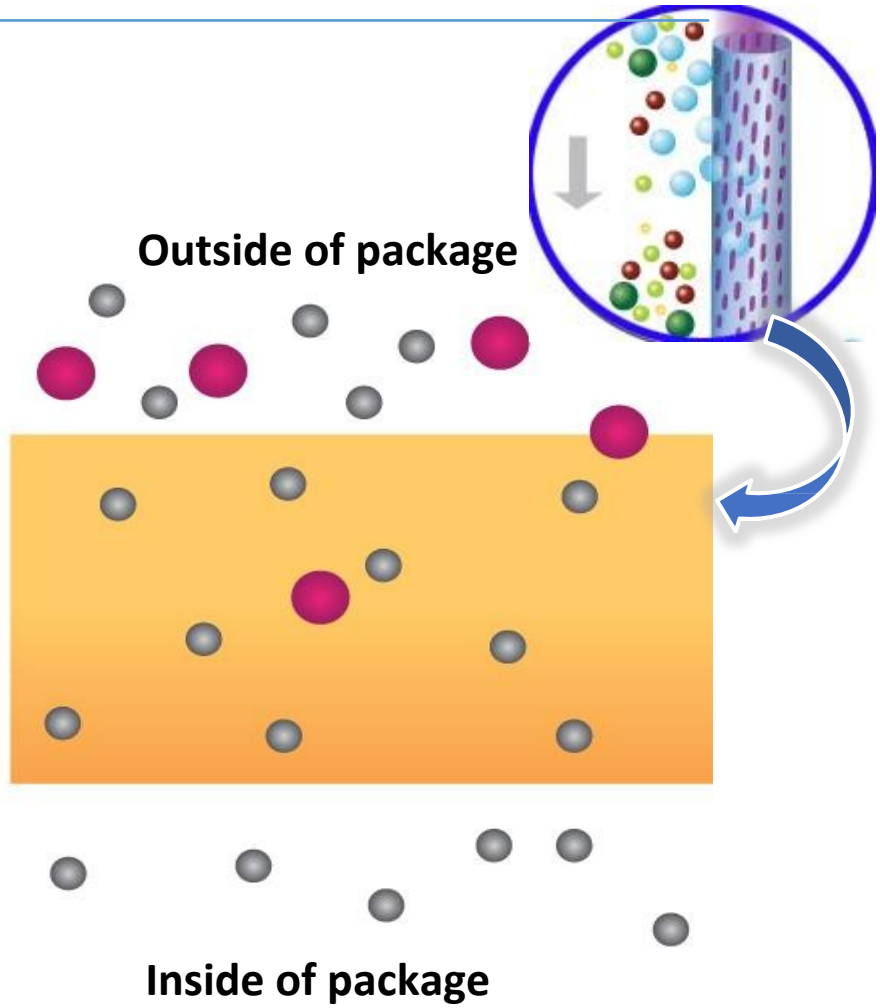
1. **Enhance polymer barrier properties;**
2. **Stronger ;**
3. **More flame resistant;**
4. **Possess better thermal properties (**E:- Melting points, degradation and glass transition temperatures) **than control polymers which contain no nanoscale filler;**
5. **Alterations in surface wettability and hydrophobicity.**

(Ray et al., 2003, Kojima et al., 1993)

Permeability of PNCs

- The permeability to gases is determined by
  - **Adsorption rate of gas molecules** into the matrix at the atmosphere/polymer boundary
  - **Diffusion rate** of adsorbed gas molecules through the matrix.

(Mercera et al., 2008)



Permeability of PNCs

(cont…)

The adsorption rate is generally dependent on

- Free volume hole sizes,
- Degree of polymer motion,
- Specific polymer-polymer Polymer-gas interactions.
- Temperature and pressure

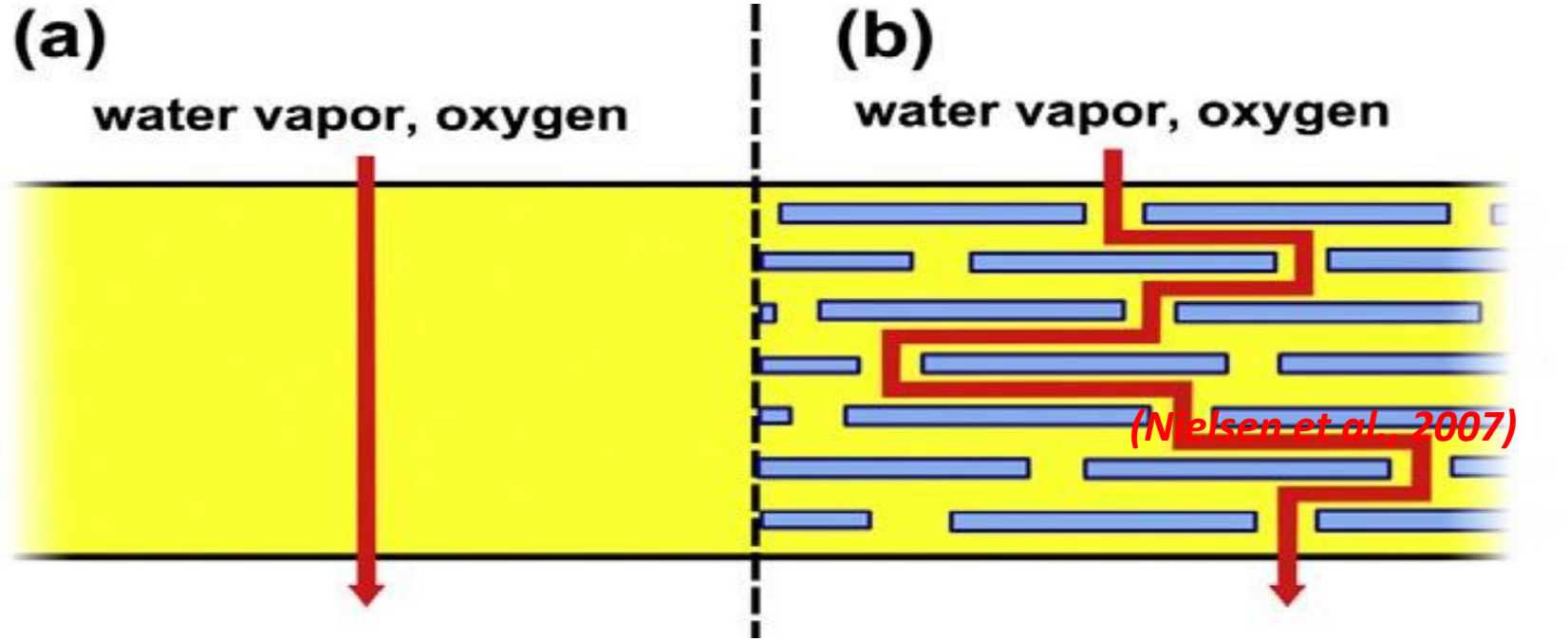
Intrinsic polymer Chemistry

Extrinsic property

Overall **gas diffusion** rate is directly dependant on the **film thickness**.

How PNCs increase barrier properties?

1. MEAN PATH LENGTH FOR GAS DIFFUSION

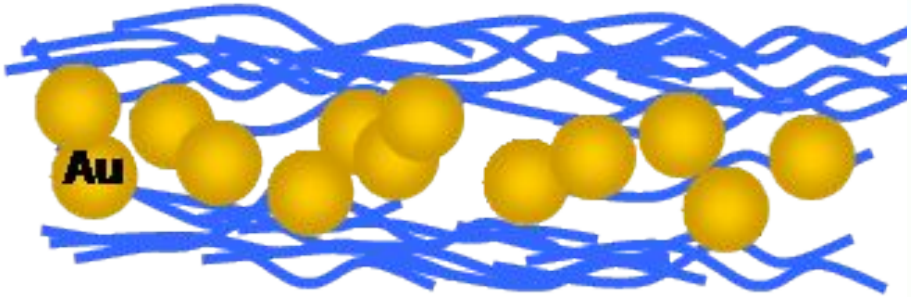


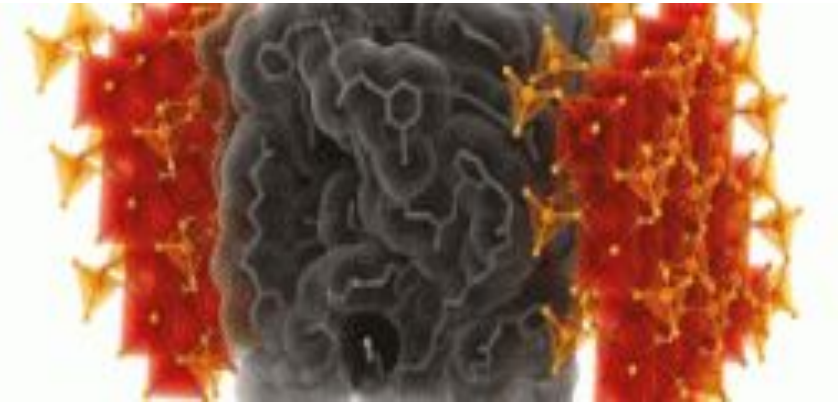
Permeability of PNCs (cont…)

2. CHANGES TO THE POLYMER MATRIX ITSELF

Beall theory- Polymer clay interface theory

- **Free volume holes,**
- **Altered density.**
- **Size of holes,**





Polymer Nanoclays and Silicates (PNCs)

(Mc Adam, 2009)

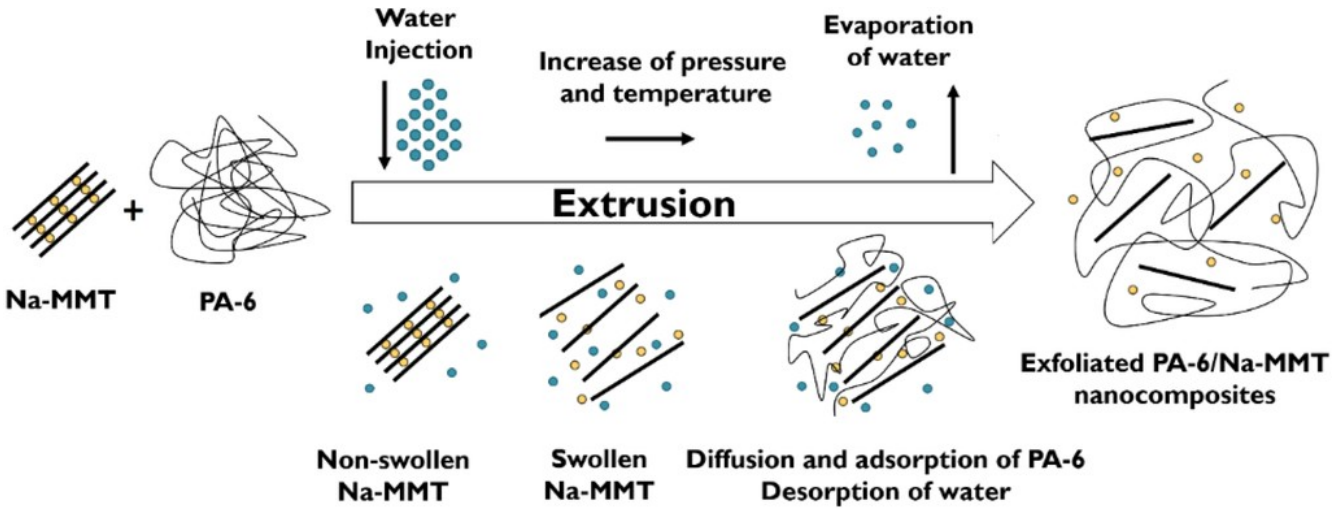
Nanoplatelets composed of clays or other silicate materials

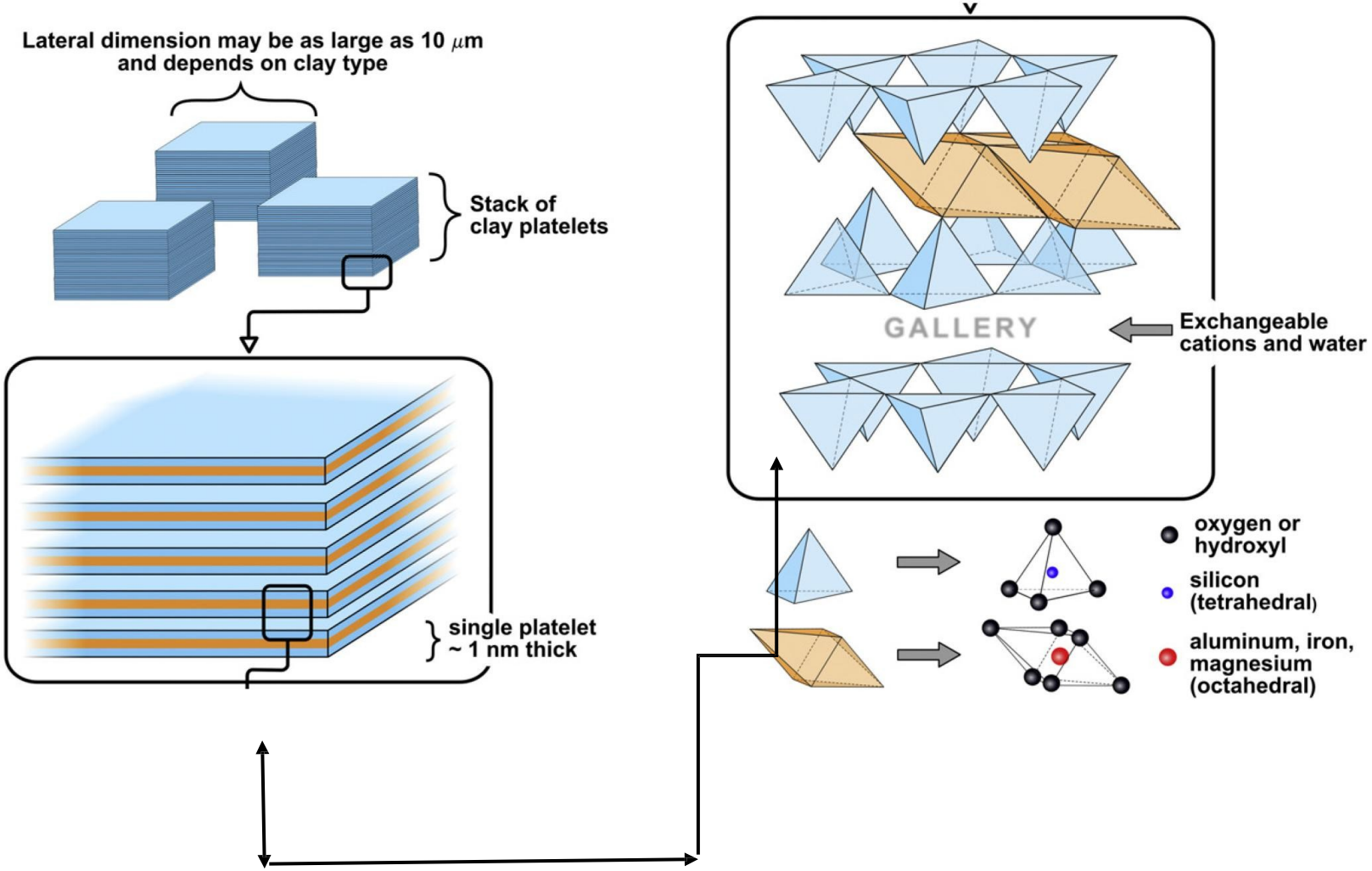
Popularity is due to

- **Low cost,**
- **Effectiveness,**
- **High stability,**
- **Benignity.**

Montmorillonite (MMT)

$$[(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_{2.}nH_2O)]$$





(Carrado, 2003)

The first successful example of a polymer–clay nanocomposite (PCNC) was a nylon-6 MMT hybrid material developed by the Toyota Corporation in 1986.

(Kawasumi, 2003)

- Kaolinite, hectrite and saponite can also be used in PNC applications.
- Water vapor permeabilities of various PNCs (**in g mm m^{-2} day^{-1}**)

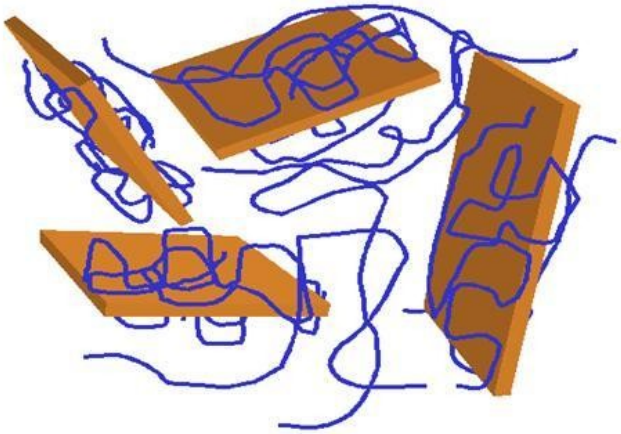
Polyamide	Polyamide nanocomposites containing 2 wt.% of			
Virgin polymer	hectrite,	saponite,	montmorillonite	Synthetic mica
12.9	12.3	10	5.86	1.16

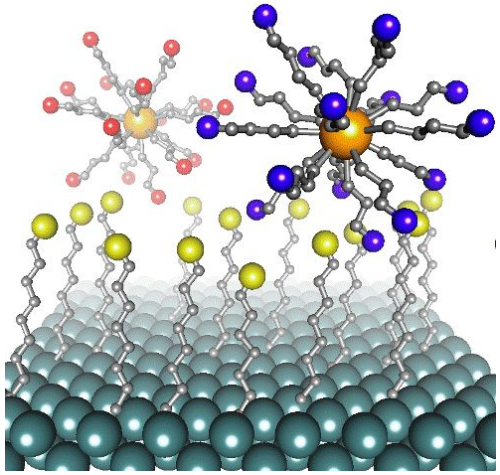
(Yano et al., 1997)

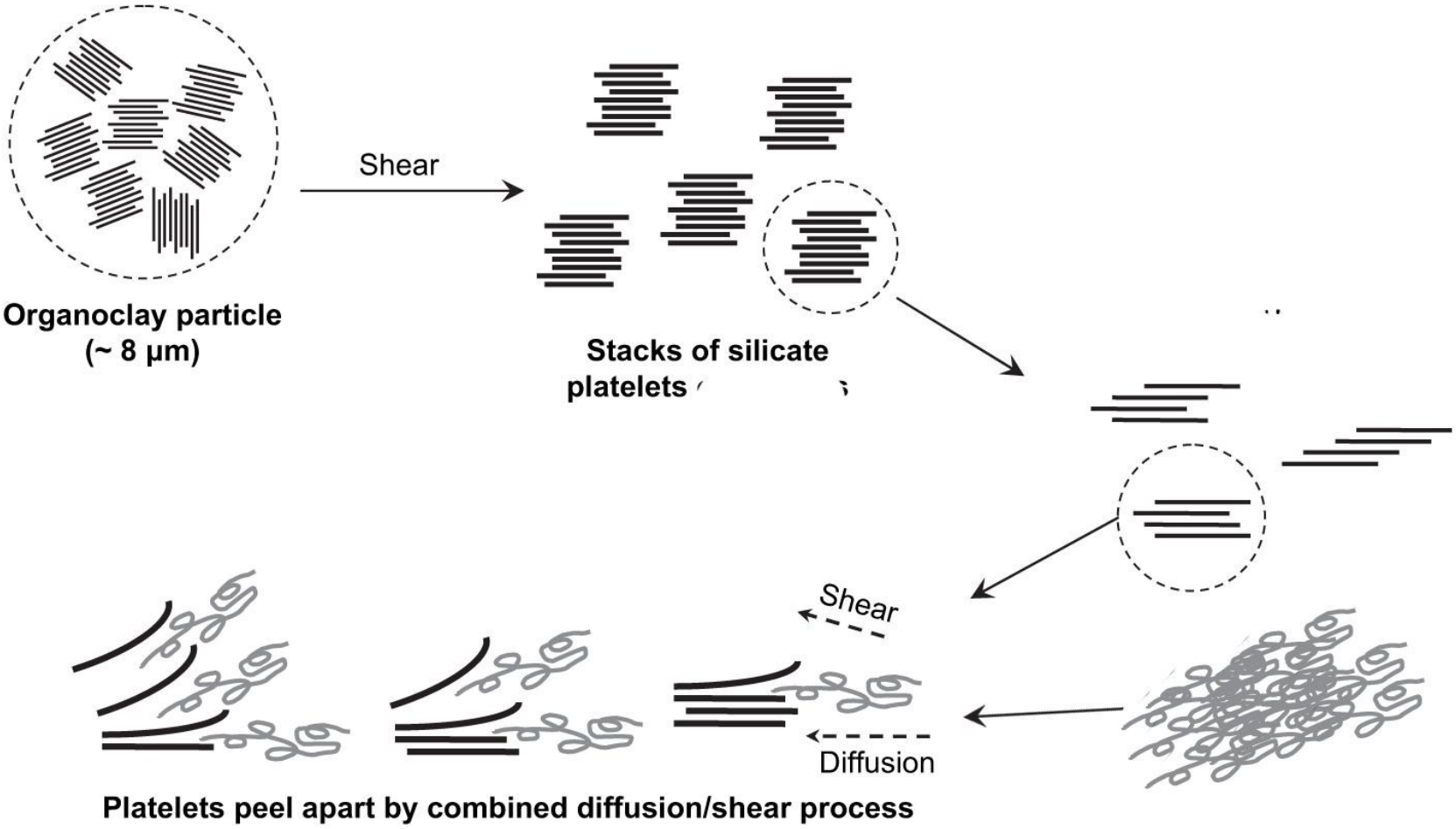
Method Preparation of PNCs

- In situ polymerization (**Kojima et al., 1999**)
- Solution method (**Ray et al., 2003**)
- Latex method (**Takahashi et al., 2006**)
- Melt processing (**Vaia et al., 1993**)
  - ✔ **Commonly used,**
  - ✔ **More economical,**
  - ✔ **More flexible**
  - ✔ **Complete exfoliation of clay particle.**

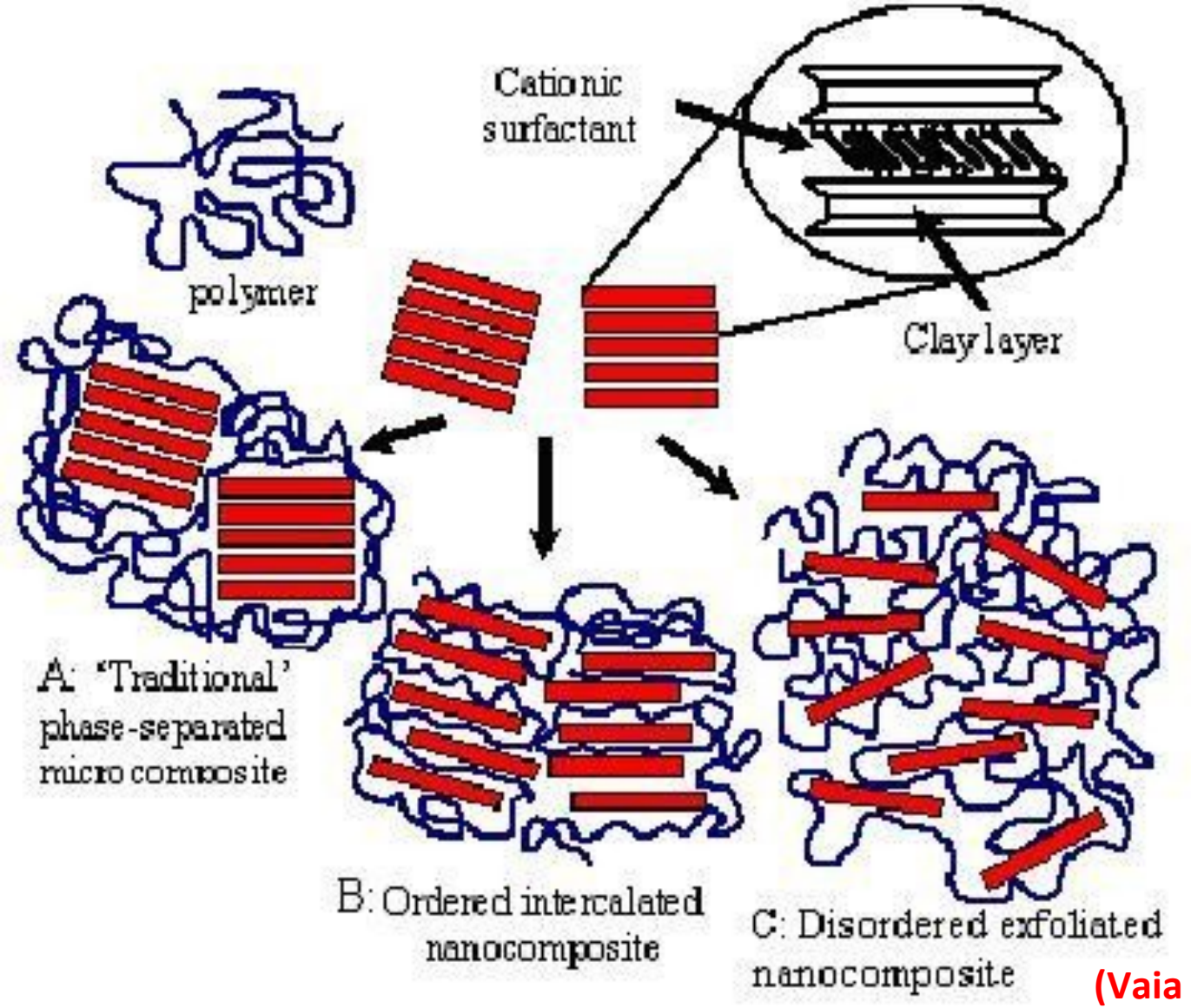
(**Picard et al., 2007**)



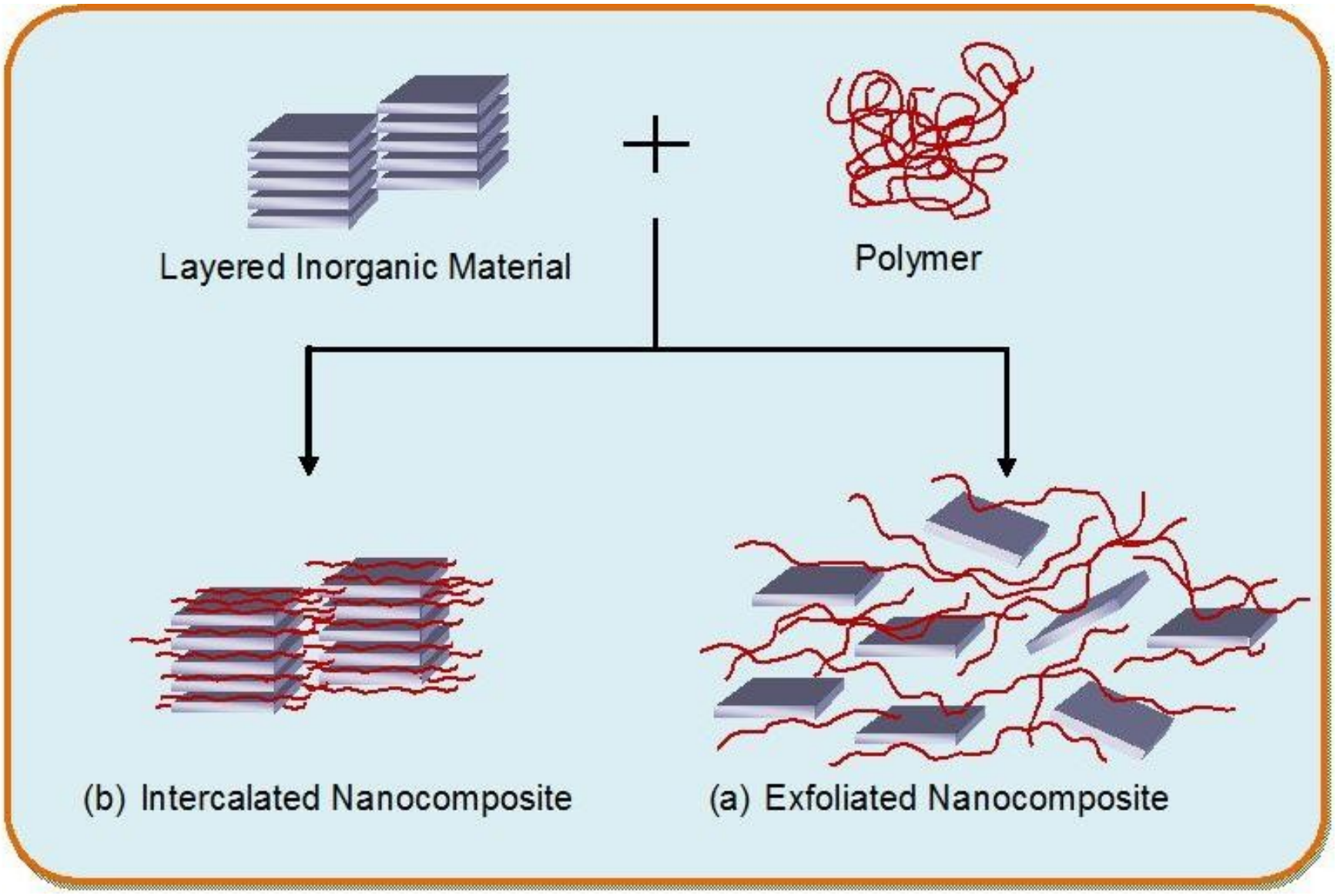




(Vaia et al., 1993)



(Vaia et al., 1993)


Layered Inorganic Material
Polymer
(b) Intercalated Nanocomposite
(a) Exfoliated Nanocomposite

2. Nano-coatings

- Incorporating nanomaterials onto the packaging surface (either the inside or the outside surface, or a sandwiched as a layer in a laminate) to improve especially the barrier properties.
- Using nano-thin coatings (polymer + nanoparticles) can help provide enhanced barrier performance.
- Vacuum-deposited aluminium coatings on plastic films.
- Coating of the surfaces of **glass food and beverage containers** (bottles, jars) with **organosilanes.**

(Smolander and choudhary 2010)

Imperm® (Nanocor Inc): in multi-layer PET bottles and sheets for improved barrier properties

Duretham® KU 2-2601 (LanXess GmbH) nylon nanocomposite for films and paper coating, designed for medium barrier applications

requiring excellent clarity

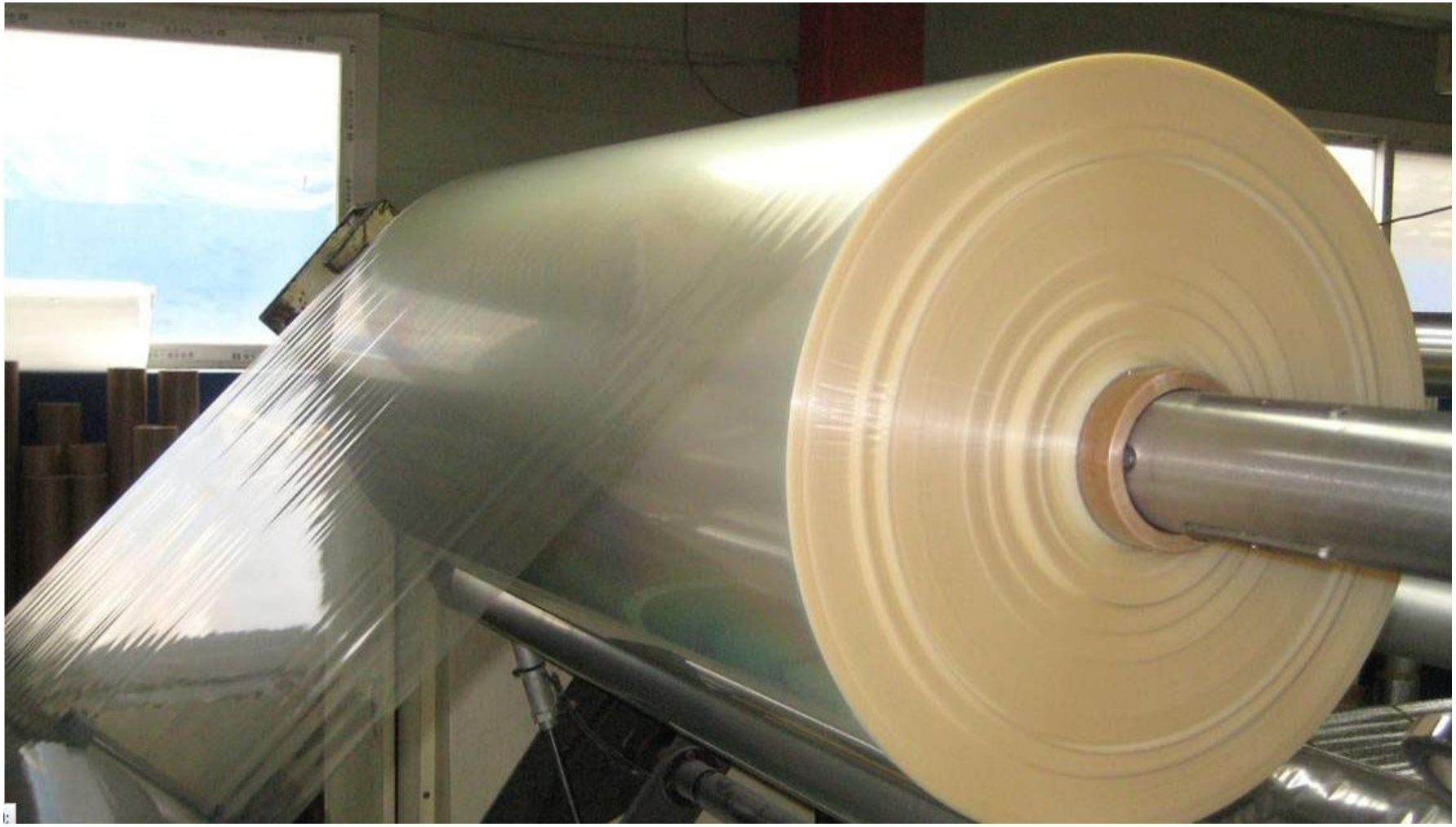
Aegis® OX (Honeywell) a polymerised nanocomposite film incorporating active O_2 scavengers and passive nanocomposite clay particles

Nano-Silica Coated High Oxygen Barrier Films

Nano-silica material is coated on base plastic films such as PET, OPP, OPA (Nylon) etc.

- **Food Packaging** **(can replace PVdC Coated Films, Oxide Evaporated films)**
  - **Processed Meat products (Beef Jerky, Rare Meat, Sausage, Ham, etc.)**
  - **Fresh Food like Rare fish, Sushi, Dried Fish, etc.**
  - **Processed milk products (Cheese, etc)**
  - **Bakery(Soft cake, Sandwich, Snack, Candy, etc.)**
  - **Nut Products with high FAT**

(Smolander and choudhary, 2010)



Nano-Silica Coated High Oxygen Barrier Nylon (OPA) Films for Food Packaging

Nano-Silica Coated High Oxygen Barrier Films **(cont…)**

Features

- Excellent Oxygen and moisture barrier,
- shelf life of packaged food increases, and hence the production cost can be decreased.
- Aroma Preservataion,
- Transparent,
- Good printablility and Laminating machinability,
- Eco-friendly (No emission of dioxin when burnt)
- Time-invariant transparency,
- Excellent mechanical and optical property (Retains the properties and characteristics of base films).

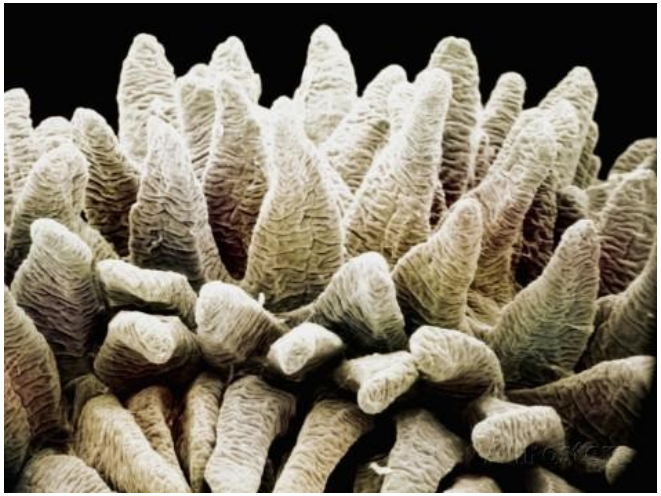
3. Surface Biocides

- Incorporating nanomaterials with antimicrobial properties on the packaging surface of packaging material.
- Used to maintain the hygienic condition of the food contact surface by preventing or reducing microbial growth and helping 'cleanability'.

Surface Biocides

(cont…)

Have a very high ratio of surface area to mass



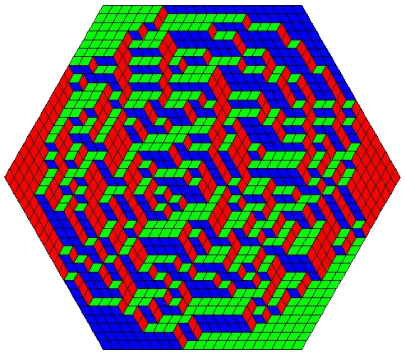
Chemicals commonly used are

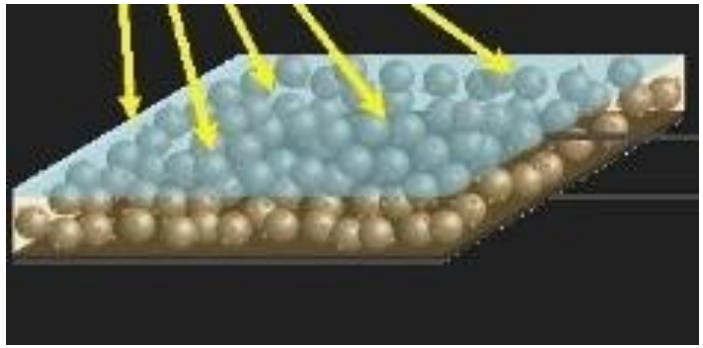
a) Nano silver (in the form of metallic silver(Ag) , $AgNO_{3,}$ etc.$_{)}$

a) Zinc oxide

b) Titanium dioxide ($TiO_{2)}$

c) Magnesium oxide

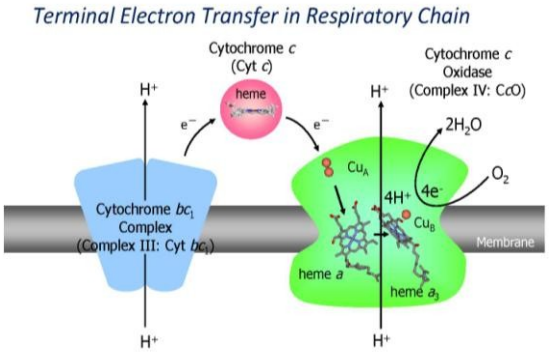


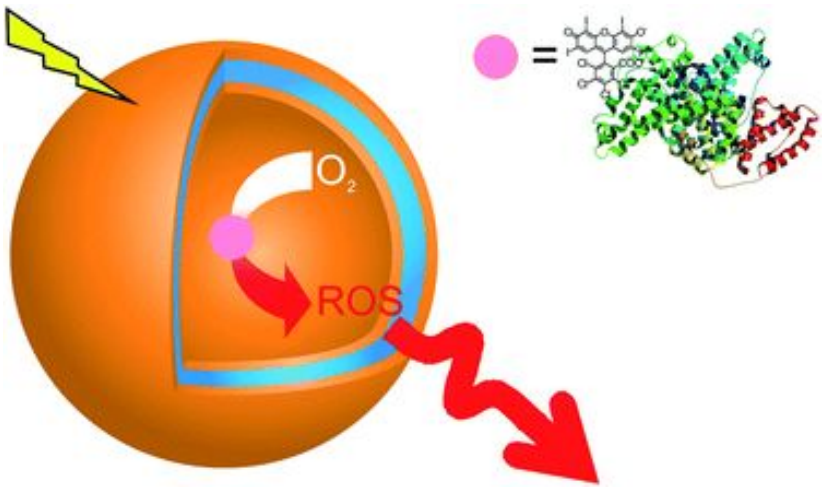


Antimicrobial activity of Nanoparticles

Activity related to several mechanisms.

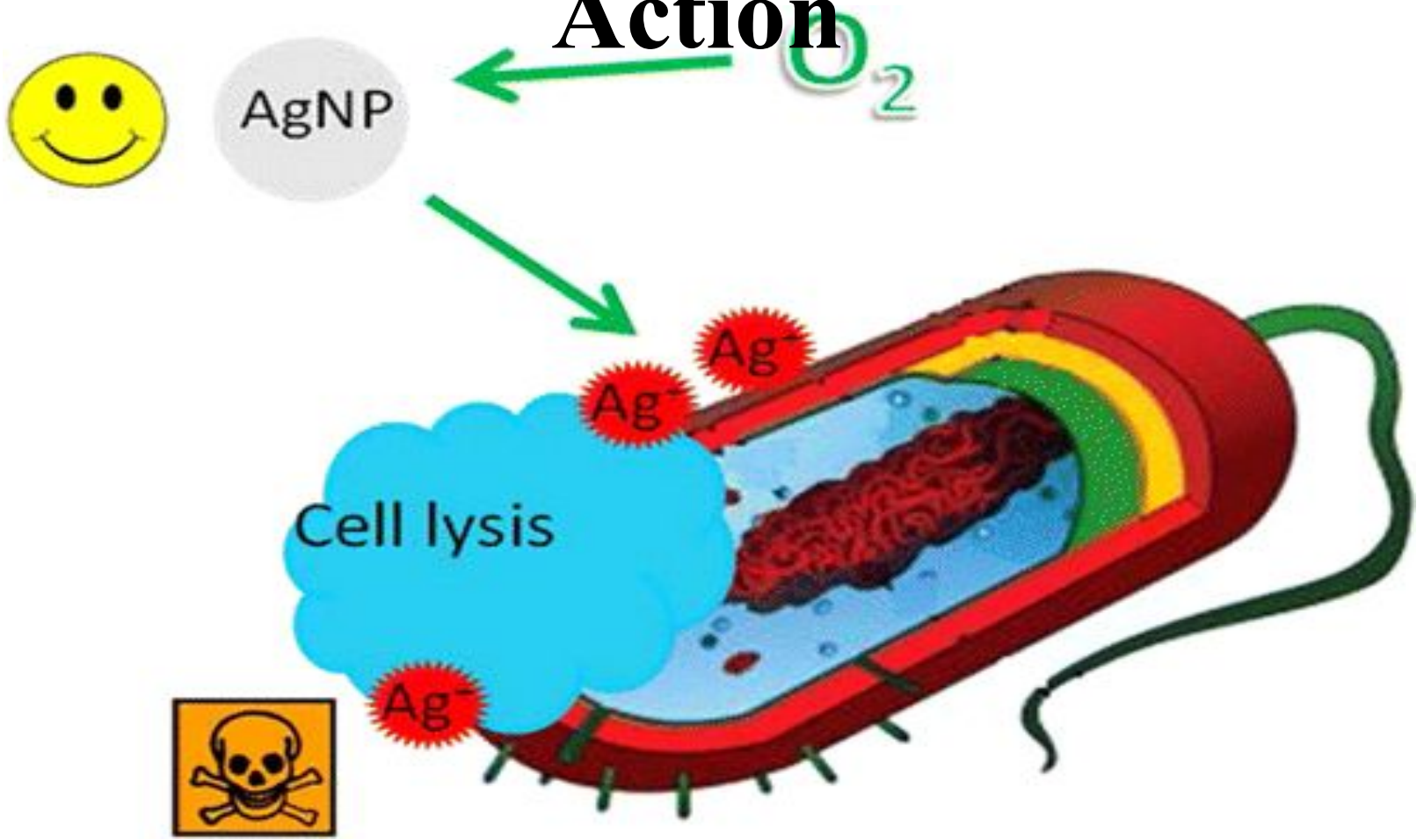
1. Directly interact with the microbial cells,
   - **a. Interrupting trans-membrane electron transfer,**
   - **b. Disrupting/penetrating the cell envelope,**
   - **c. Oxidizing cell components,**
2. By produce secondary products
   - **a. Reactive oxygen species (ROS)**





(*Li et al., 2008*)

Mechanism of Action



Nanomaterial with Titanium Oxide

- Non-toxic and has been approved by the American Food and Drug Administration (FDA)
- Bactericidal and fungicidal effects
- Act against *E. coli*, *Salmonella choleraesuis*, *Vibrio parahaemolyticus*, *Listeria monocytogenes*, *Pseudomonas aeruginosa*, *Stayphylococcus aureus*, *Diaporthe actinidiae* and *Penicillium expansum*. **(Chawengkijwanich & Hayata, 2008)**

Environ Sci Technol. 2012 Feb 21; 46(4): 2242–2250.
Published online 2012 Feb 8. doi: 10.1021/es2041684

Titanium Dioxide Nanoparticles in Food and Personal Care Products

Alex Weir,[1] Paul Westerhoff,[1,*] Lars Fabricius,[2,3] and Natalie von Goetz[2]

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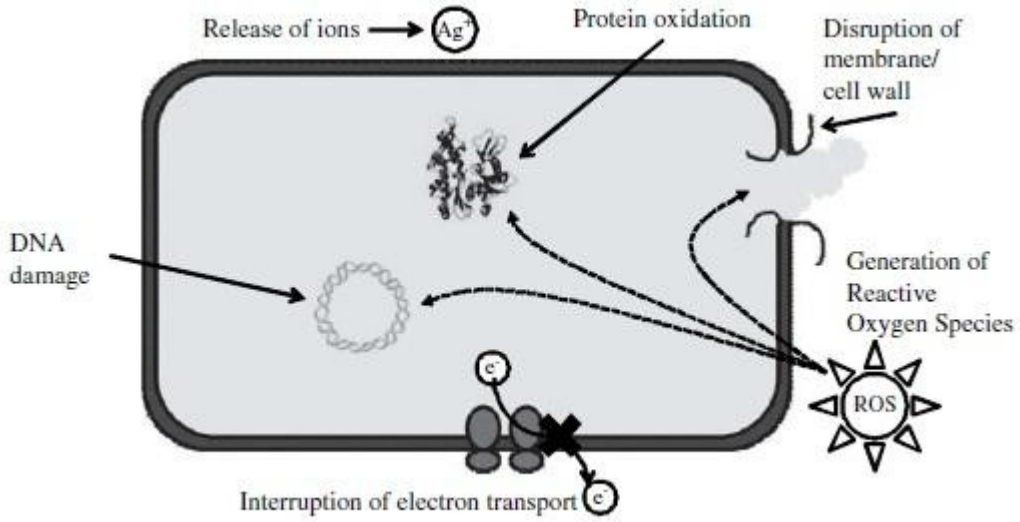
Abstract Go to:

Titanium dioxide is a common additive in many food, personal care, and other consumer products used by people, which after use can enter the sewage system, and subsequently enter the environment as treated effluent discharged to surface waters or biosolids applied to agricultural land, incinerated wastes, or landfill

Nanomaterial with ZnO

- Can efficiently kill on contact both Grampositive and Gram-negative bacteria . (***Jones et al., 2008***).
- Nano-ZnO coated films exhibits antimicrobial effects against *L.monocytogenes* and *S.enteritidis* in liquid egg white and in culture media (***Jin et al., 2009***)
- Currently listed by FDA as a generally recognized as safe (GRAS) material.

packaging.



4. Active Nano-packaging

Incorporating nanomaterials with antimicrobial or other properties (e.g. antioxidant) with intentional release into- packaged food. and consequent effect on the

(Bradley et al., 2011)

1. Antimicrobial agents like AgNPs , magnesium oxide, copper and copper oxide, zinc oxide, cadmium selenide/telluride, chitosan and carbon nanotubes are used.

- Ultrasonically dispersed TiO_2 nanoparticles throughout EVOH films observed their effective photo-activated biocidal and properties microorganisms (bacteria and yeasts) against

(Kim et al., 2003)

AgNPs being incorporated into cellulose pads for use in modified atmosphere packaging of fresh beef.

(Fernandaz et al., 2010)

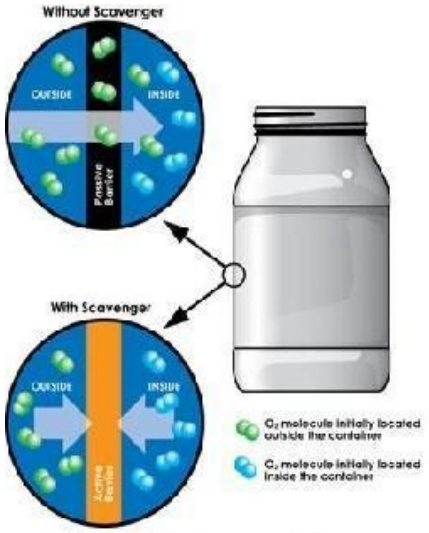
Active Nano-packaging (cont…)

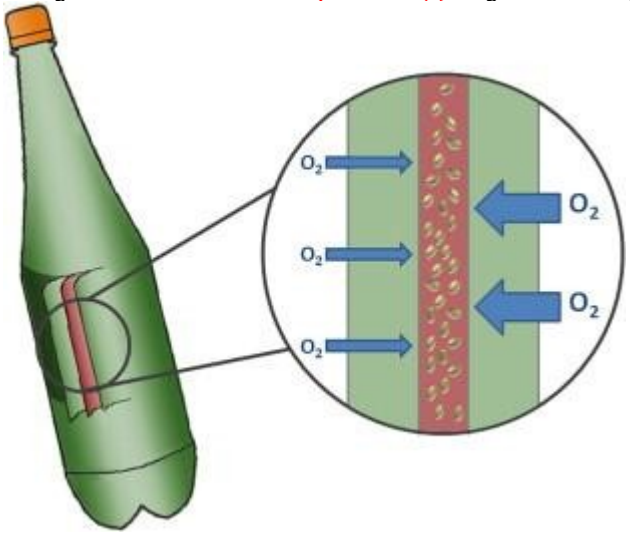
2. Oxygen Scavenging Materials

- Food deterioration by indirect action of O_2 includes food spoilage by aerobic microorganisms.

(Xiao-e, Green, Haque, Mills, & Durrant, 2004).

- Oxygen scavenger films were successfully developed by **Xiao et al. (2004)**, by adding

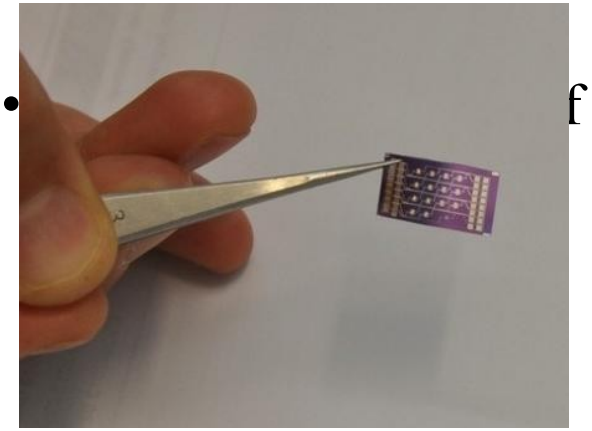


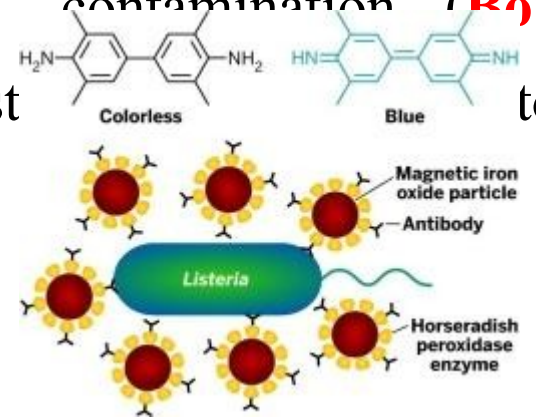


5. Intelligent Packaging

Incorporating nanosensors to monitor and report on the condition of the food.

- They are able to respond environmental changes inside the package (Temperature, humidity and level of oxygen exposure)
  - Nanosensers communicate the degradation of product or microbial contamination (Bouwmeester et al., 2009)
- f st tor





Nanosensors in Packaging

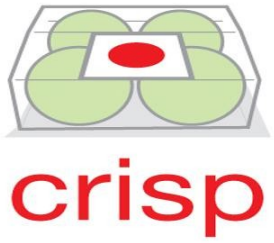
- Nanosensors can detect certain chemical compounds, pathogens,and toxins in food,
- Eliminate the need for inaccurate expiration dates,
- Providing real-time status of food freshness **(Liao, Chen, & Subramanian, 2005)**.

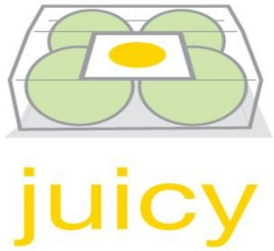
Eg. Ripesense, onvu

(www.ripesense.com, www.onvu.com)

OnVu™ –TO ENSURE THE COLD

Now you can choose your perfect pear by its colour.

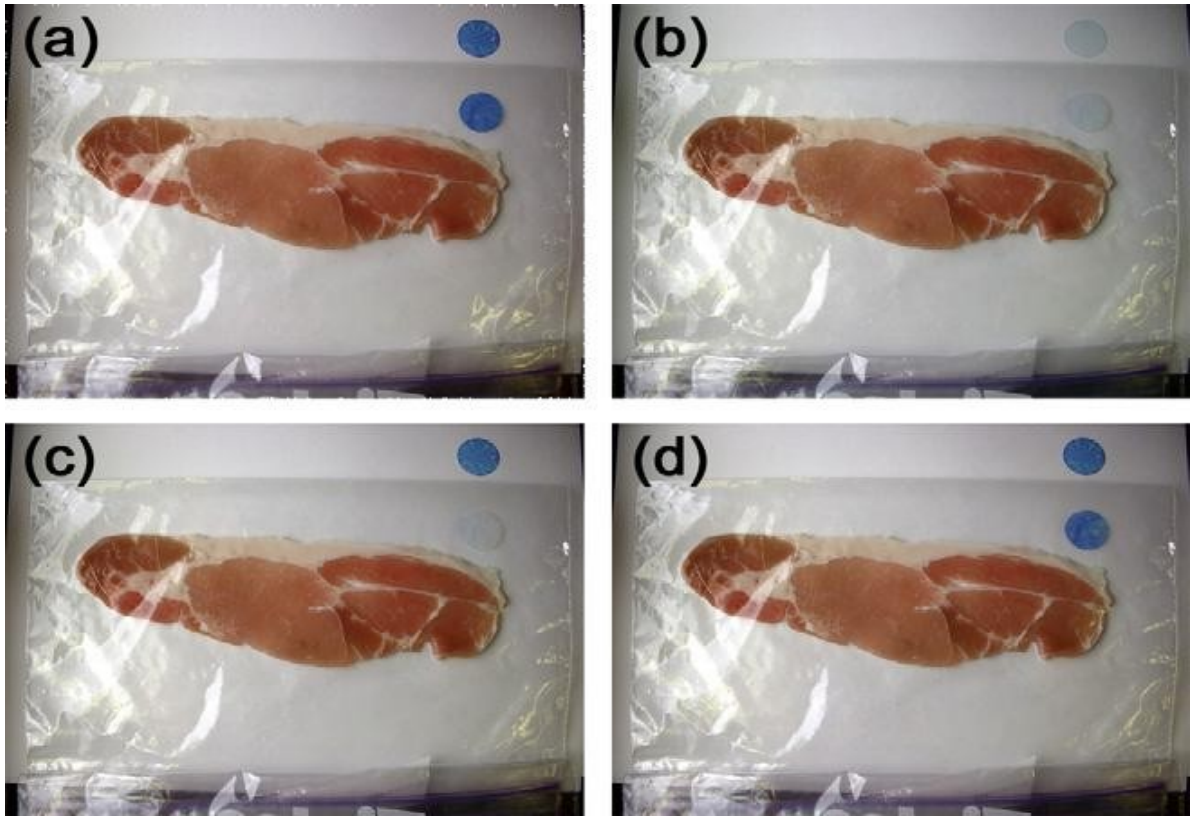




Nanosensors in Packaging

Examples of Nanosensors in Packaging

1.Noninvasive gas sensers- **Mills et al., 2005)** Photoactivated indicator ink for in-package oxygen detection based upon Nano sized TiO_2 or SnO_2 particles and a redox-active dye (methylene blue).

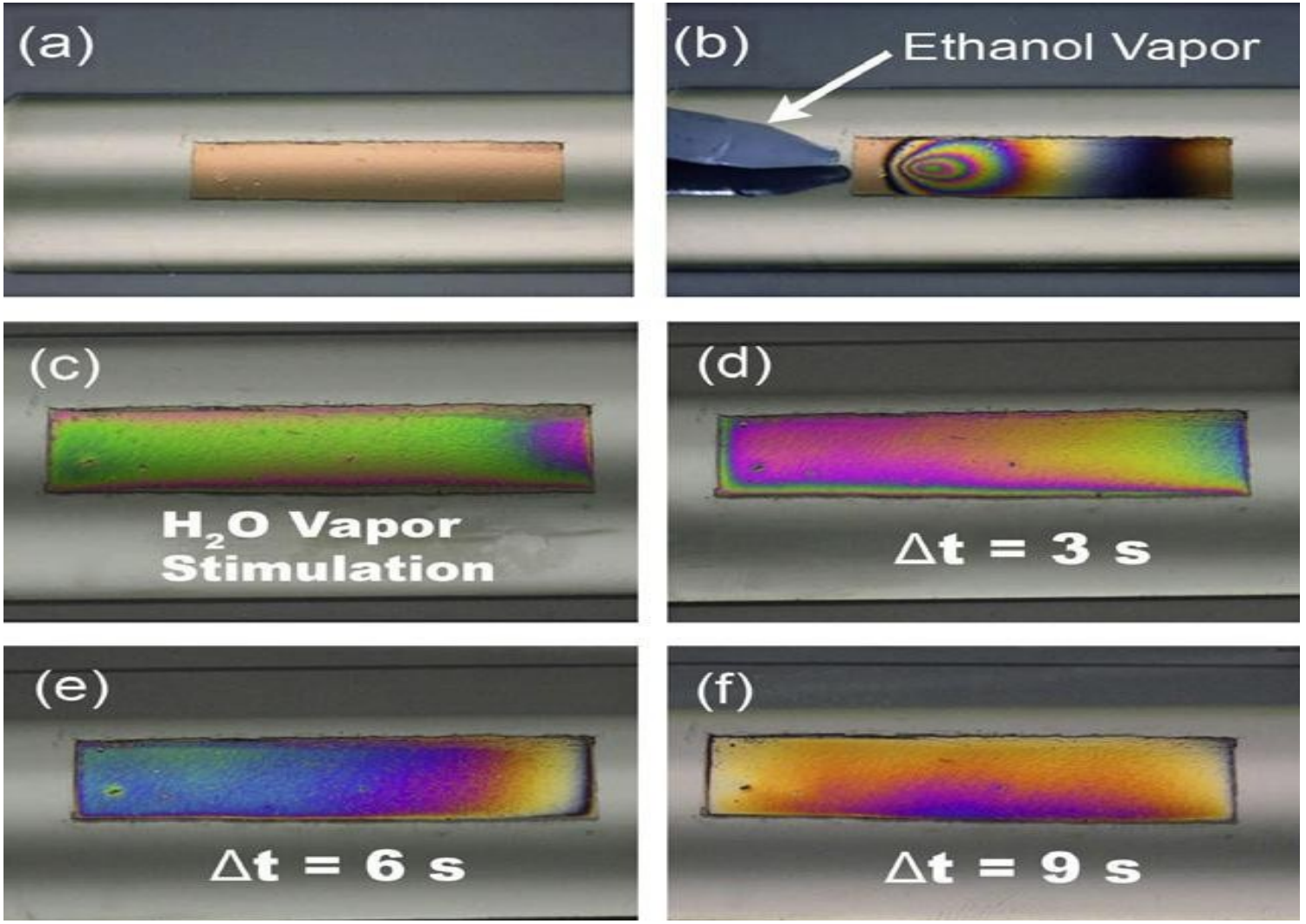


(www.dx.doi.org/10.1039/B503997P)

2. Sensor for moisture content-

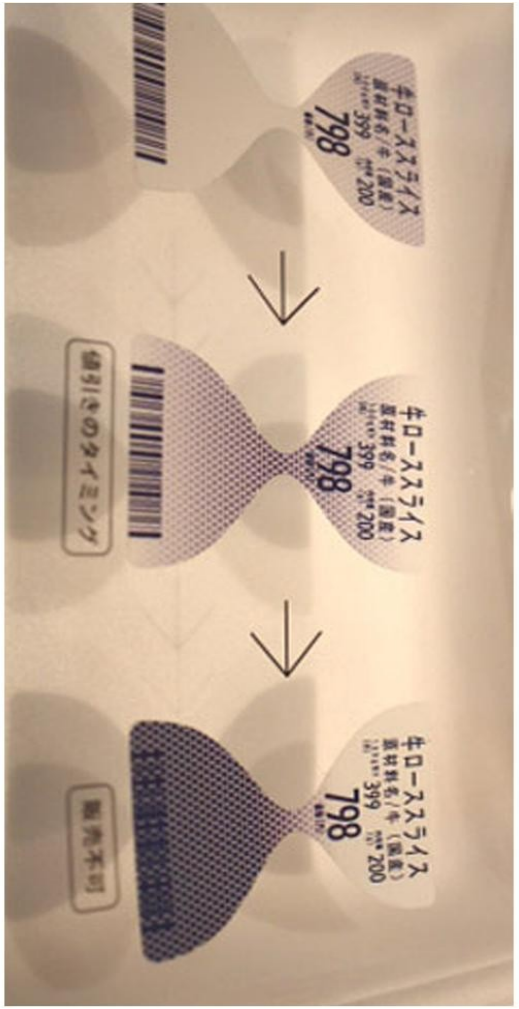
(Luechinger et al., 2007)

Based upon carbon-coated copper nanoparticles dispersed in a tenside film.



3. Carbon dioxide content in MAPs- (McEvoy et al., 2006)

Based upon analysis of luminescent dyes standardized by fluorophore-encapsulated polymer Nano beads http://www.nextnature.net



6. Bio-plastics

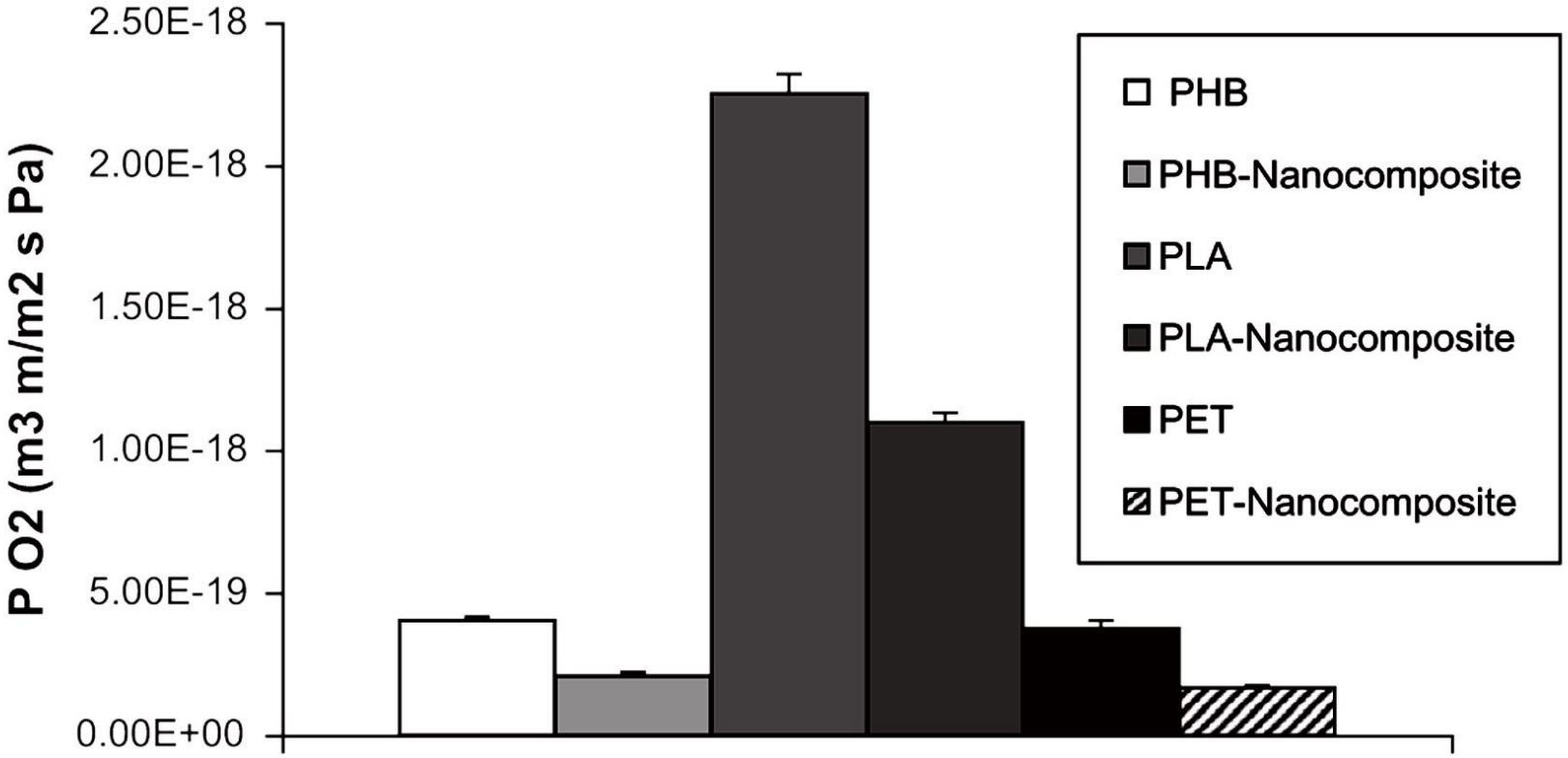
- Biodegradable polymers, which meet all criteria of scientifically recognized norms for biodegradability and compostability.
- Renewable biomass source such as vegetable oil, corn-starch, potato-starch or microbia, rather than fossil- fuel plastics which are derived from petroleum.
- **Polylactic Acid (PLA) plastics**
- **Polyamides 11**

(Cabedo, et al. 2005)

Advantages of Bio-plastics with nanoparticle

- Increase the gas and vapour barrier properties,
- Better biodegradability,
- Increase the mechanical properties and thermal stability,
- Efficient antioxidant, oxygen scavenging or antimicrobial bio packaging,
- Increased foods quality and safety

(Garcia et al., 2007)



Oxygen permeability of PLA, PHB and PET and of their nanocomposites (Sanchez-Garcia *et al.*, 2007).

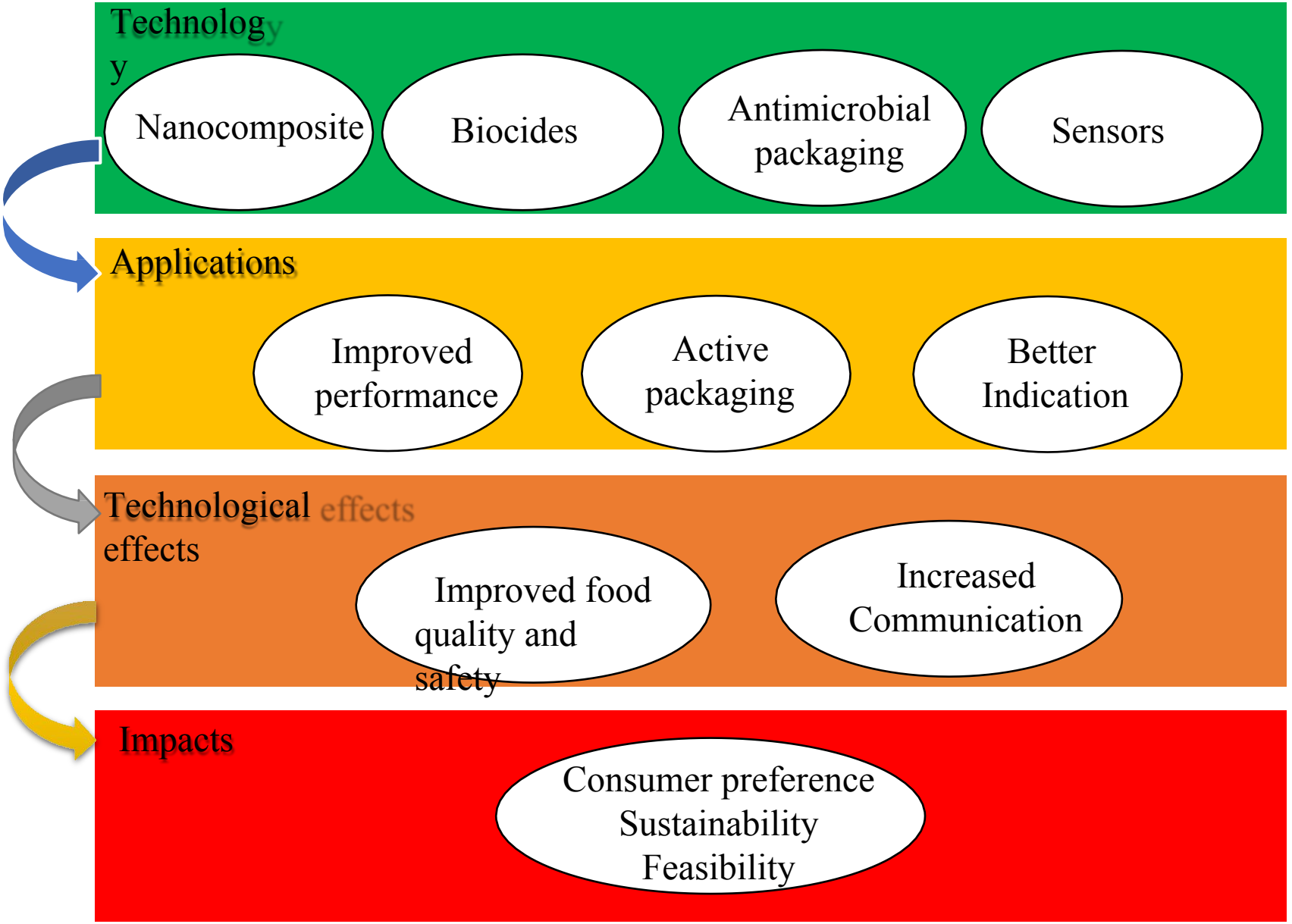
Safety Issues

- Food safety and quality and impact on consumers
- Environmental impact

- Possible migration into food and drinks causing a toxicological risk.
- Fate in the environment after disposal of the packaging.
- Fate during recovery and recycling to make ‘new’ packaging materials.

Uncertainties in consumer safety and environmental safety

- Lack of understanding on how to evaluate the potential hazard of nanomaterials by the oral (food) route.
- Lack of tools to use to estimate exposure.
- Possibility that the high surface area and active surface chemistry of some nanomaterials could give rise to unwanted chemical reactions.
- Lack of understanding on the impact of nanomaterials in waste disposal


Technology
Nanocomposite
Biocides
Antimicrobial packaging
Sensors
Applications
Improved performance
Active packaging
Better Indication
Technological effects
Improved food quality and safety
Increased Communication
Impacts
Consumer preference
Sustainability
Feasibility


Thank you
60 seconds to heat
240 ml
ml
140
120
100
80
60
40
Thank you
two new teats