Review of Active Solutions for Packaging Applications

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We develop new smart technologies, profitable solutions and innovative services. We cooperate with our customers to produce technology for business and build success and well-being for the benefit of society.

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- Turnover 272 M€
  Personnel 2,470
- Unique research and testing infrastructure
- Wide national and international cooperation network

VTT on the map

VTT's locations in Finland

Personnel by location

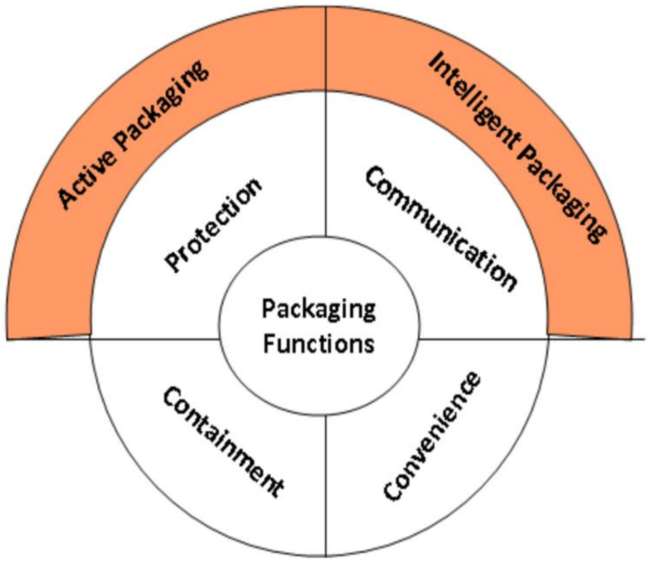
	VTT Group	Parent company
Espoo	1,674	1,484
Jyväskylä	92	72
Kuopio	26	13
Oulu	315	314
Sodankylä	29	-
Tampere	249	232
Other locations	29	13
Total	**2,414**	**2,128**

VTT's international research units
Seoul (South Korea)

VTT's marketing and networking offices
Brussels (Belgium)

Active Packaging	
Releasers	**Absorbers**
preservatives	oxygen
flavours	moisture
antioxidants	ethylene
cabon dioxide	carbon dioxide
ethylene	odour

Intelligent Packaging
time temperature indicators
oxygen indicators
humidity indicators
carbondioxide indicators
spoilage indicators



Kalite Sistem Group
Affiliated to the Austrian Agency for Health and Food Safety

Demand for **active and intelligent** packaging in the U.S. is forecast to expand 8.0 percent annually to **3.1 billion €** in 2017, well above total packaging demand growth.

Active packaging demand is expected to increase 5.7 percent annually to **2.0 billion €** in 2017.

ACTIVE & INTELLIGENT PACKAGING DEMAND
(million dollars)

Item	2007	2012	2017	% Annual Growth 2007-2012	2012-2017
Active & Intelligent Packaging Demand	1308	2370	3480	12.6	8.0
Active Packaging:	1230	1635	2160	5.9	5.7
Gas Scavengers	384	610	870	9.7	7.4
Corrosion Control Packaging	374	405	485	1.6	3.7
Moisture Control Packaging	281	348	425	4.4	4.1
Other	191	272	380	7.3	6.9
Intelligent Packaging	78	735	1320	56.6	12.4

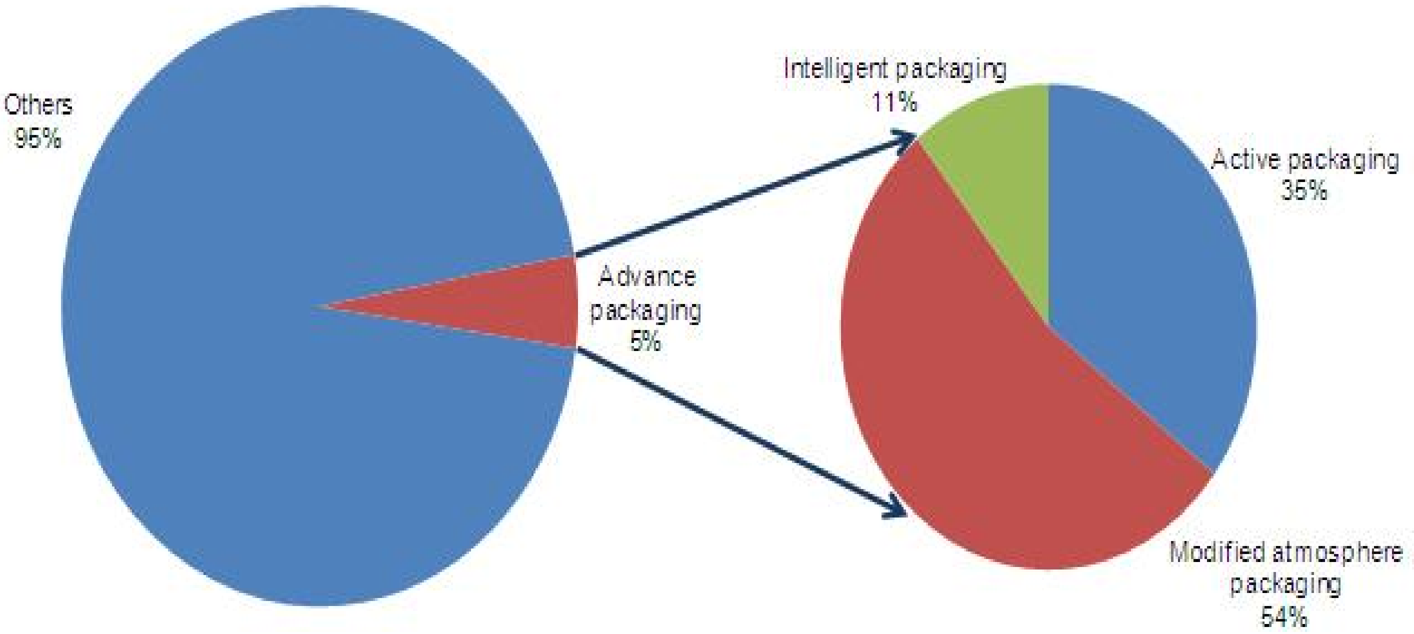


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Table 1. Active packaging technologies and mechanisms [6,8,9,10,12,14].

Active packaging	Active substances and mechanisms
Oxygen scavenger	Iron powder, ferrous carbonate, ascorbic acid, polyunsaturated polymers, ethylene methacrylate and cyclohexene methacrylate, benzyl acrylate, ascorbate, MXD-6 (aromatic polyamide) oxidation, enzymes (glucose oxidase, catalase, alcohol oxidase, superoxide dismutase), sulphites, unsaturated fatty acids (oleic, linoleic, linolenic), immobilization of yeasts in solid holders, photosensitive dyes, butylated hydroxytoluene (BHT), vitamins E and C, transition metal catalysts (platinum, cobalt, copper), rice extracts, catechol
Carbon dioxide scavenger	Calcium hydroxide, sodium hydroxide, potassium hydroxide, zeolites, active carbon
Carbon dioxide emitter	Ferrous carbonate, ascorbic acid, sodium bicarbonate
Ethylene scavenger	Potassium permanganate, palladium catalyst, zeolites, clays, Oya-stone, active carbon, silica gel, metallic oxides, tetrazine
Moisture scavenger	Silica gel, zeolites, propyleneglycol, calcium, barium and magnesium oxides, calcium sulphate, natural clays (such as montmorillonite), different salts, polyvinyl alcohol, molecular sieves, glycerol, polyacrylate salts, graft copolymers of starch
Ethanol emitter	Encapsulated ethanol, ethanol vapour generators

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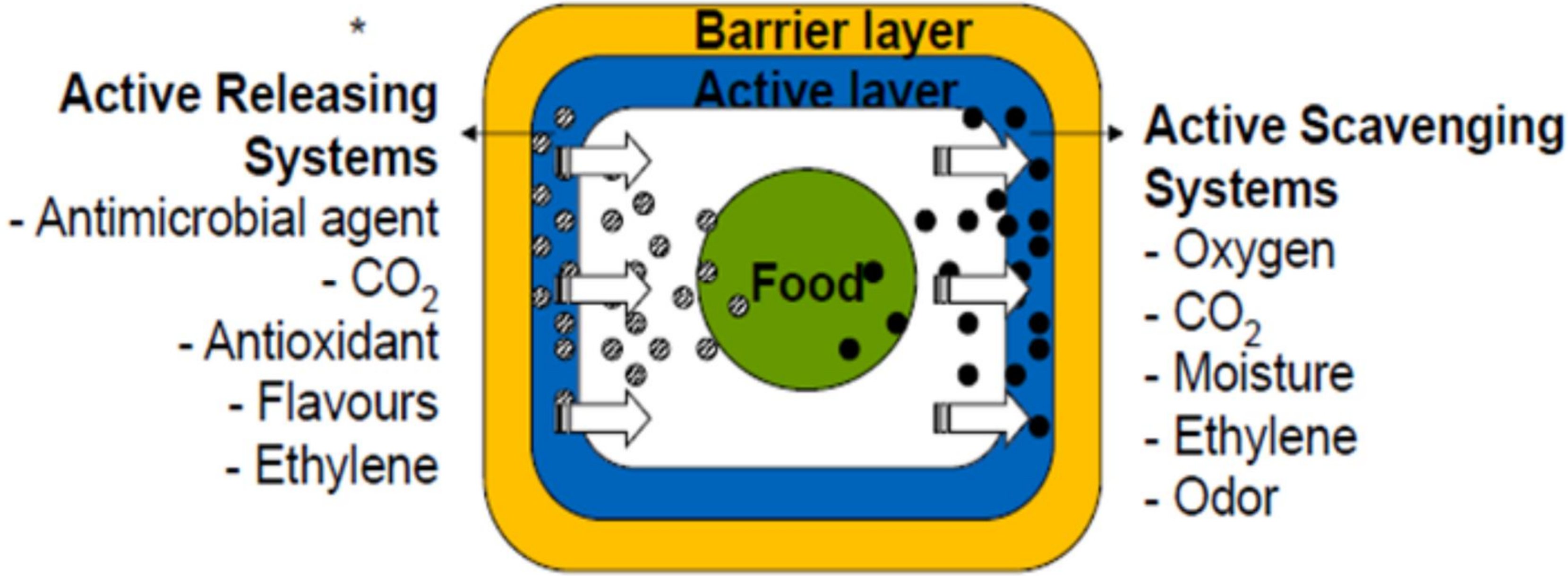
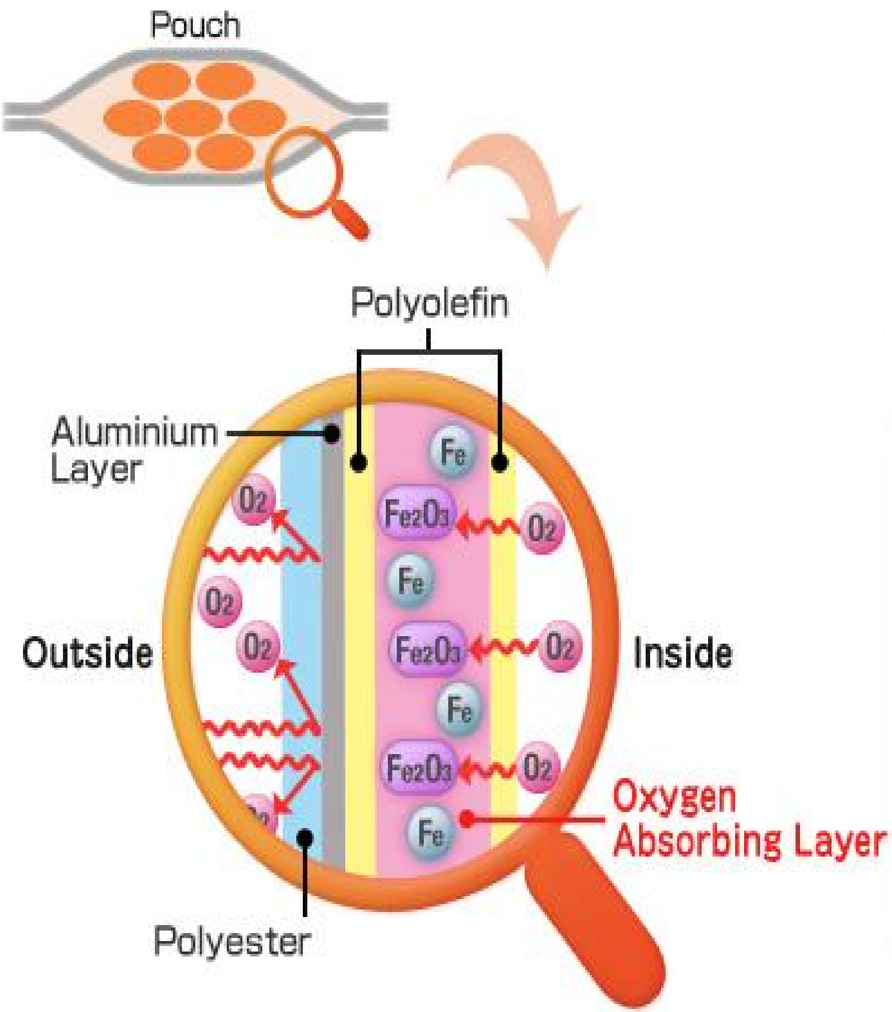
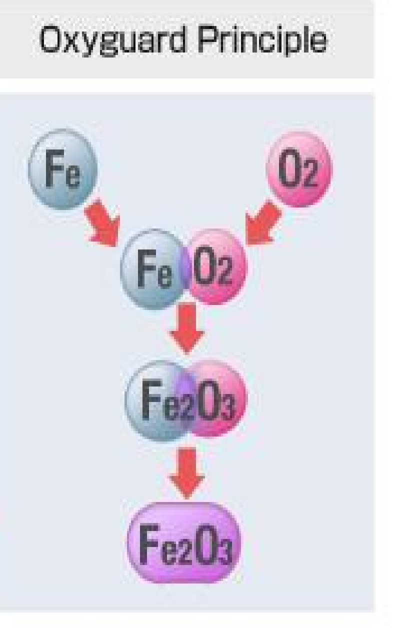
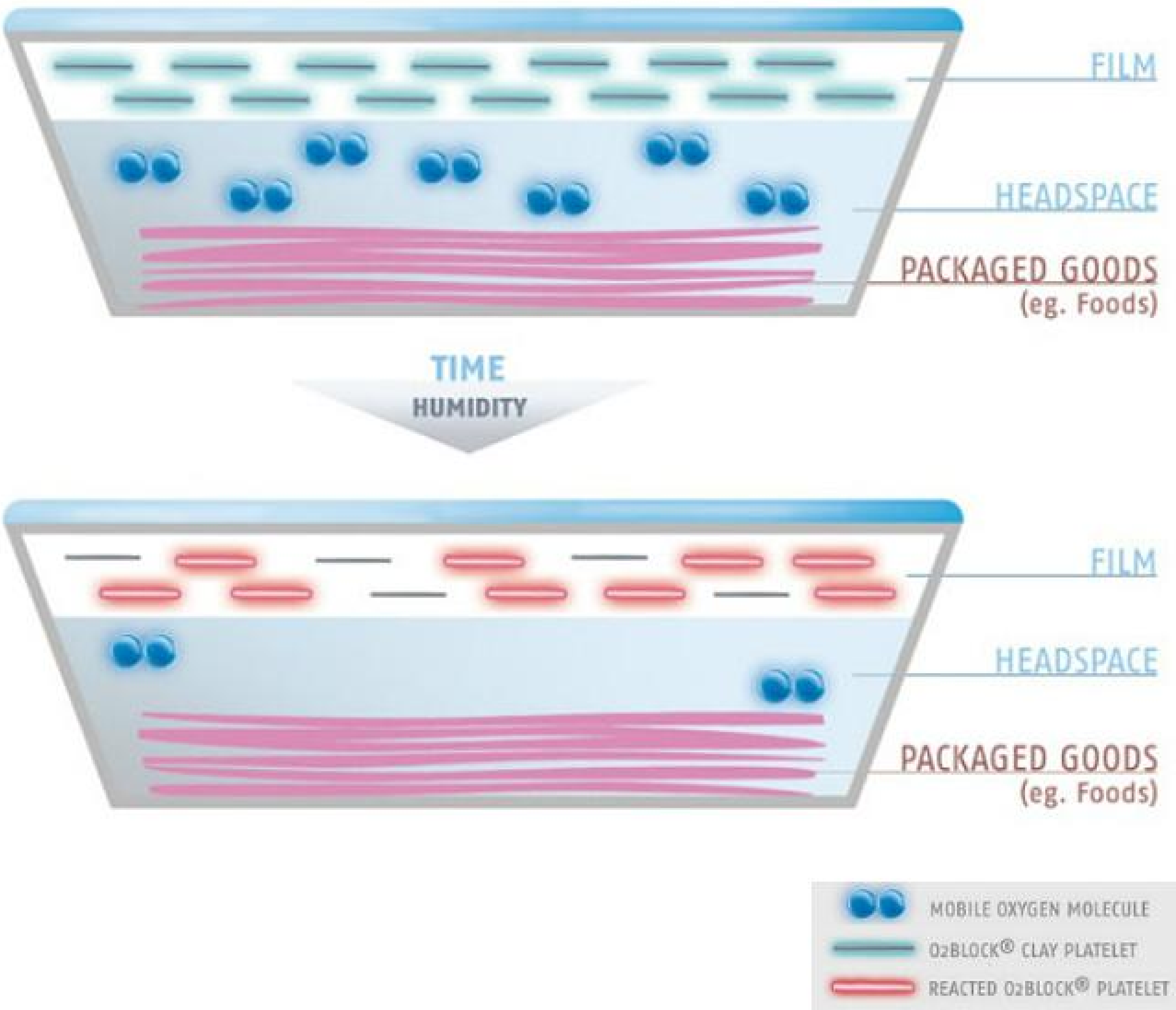


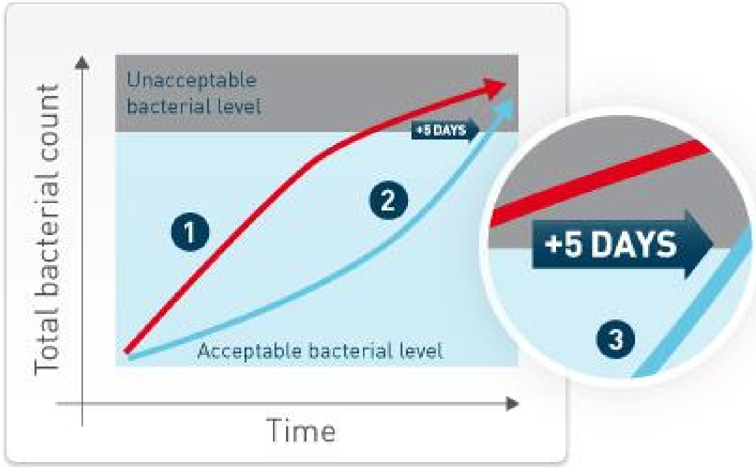
Yildirim, S. Newsletter Transfer, 3-2010, Wädenswil, Switzerland

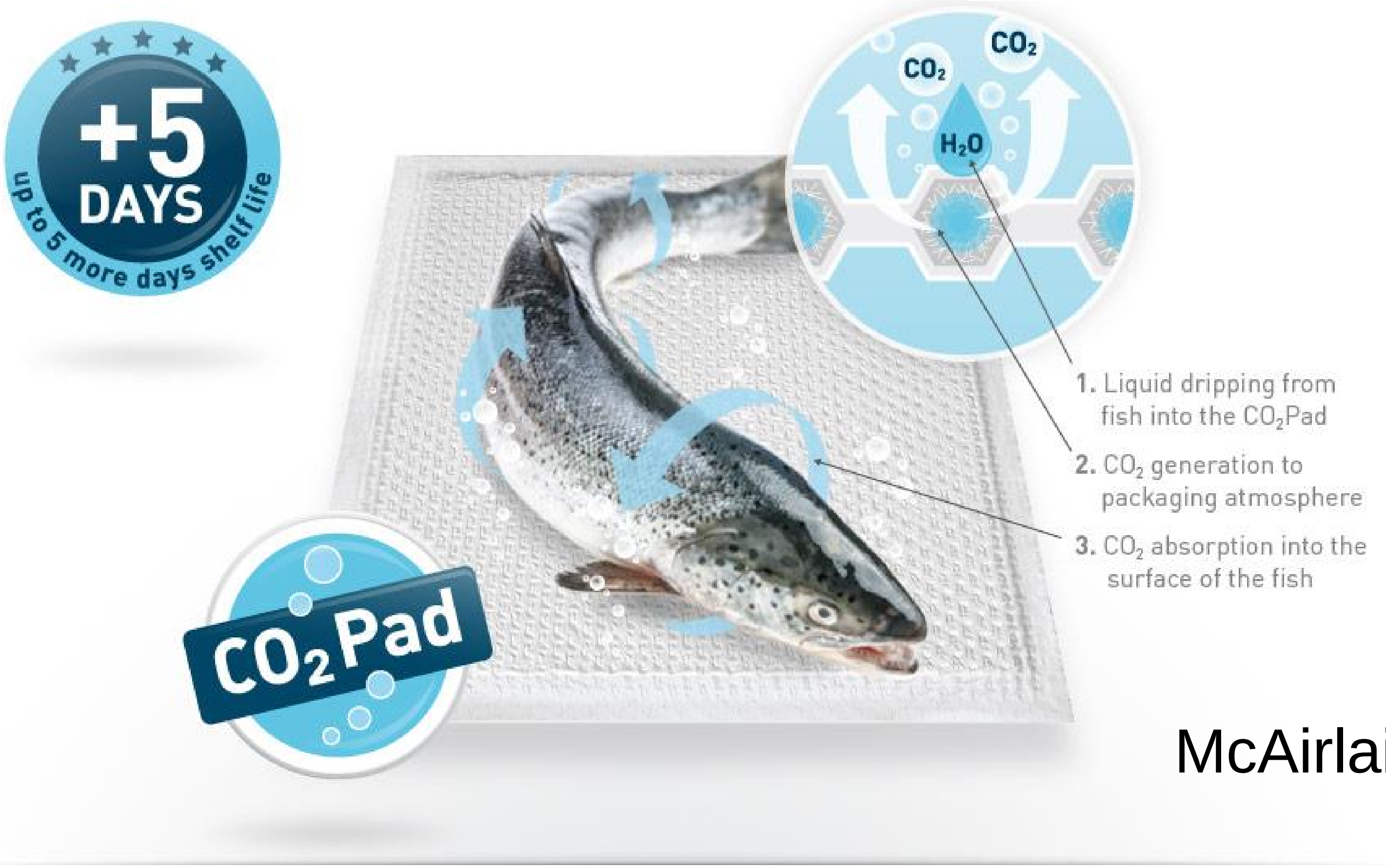
Oxygen coming from both sides



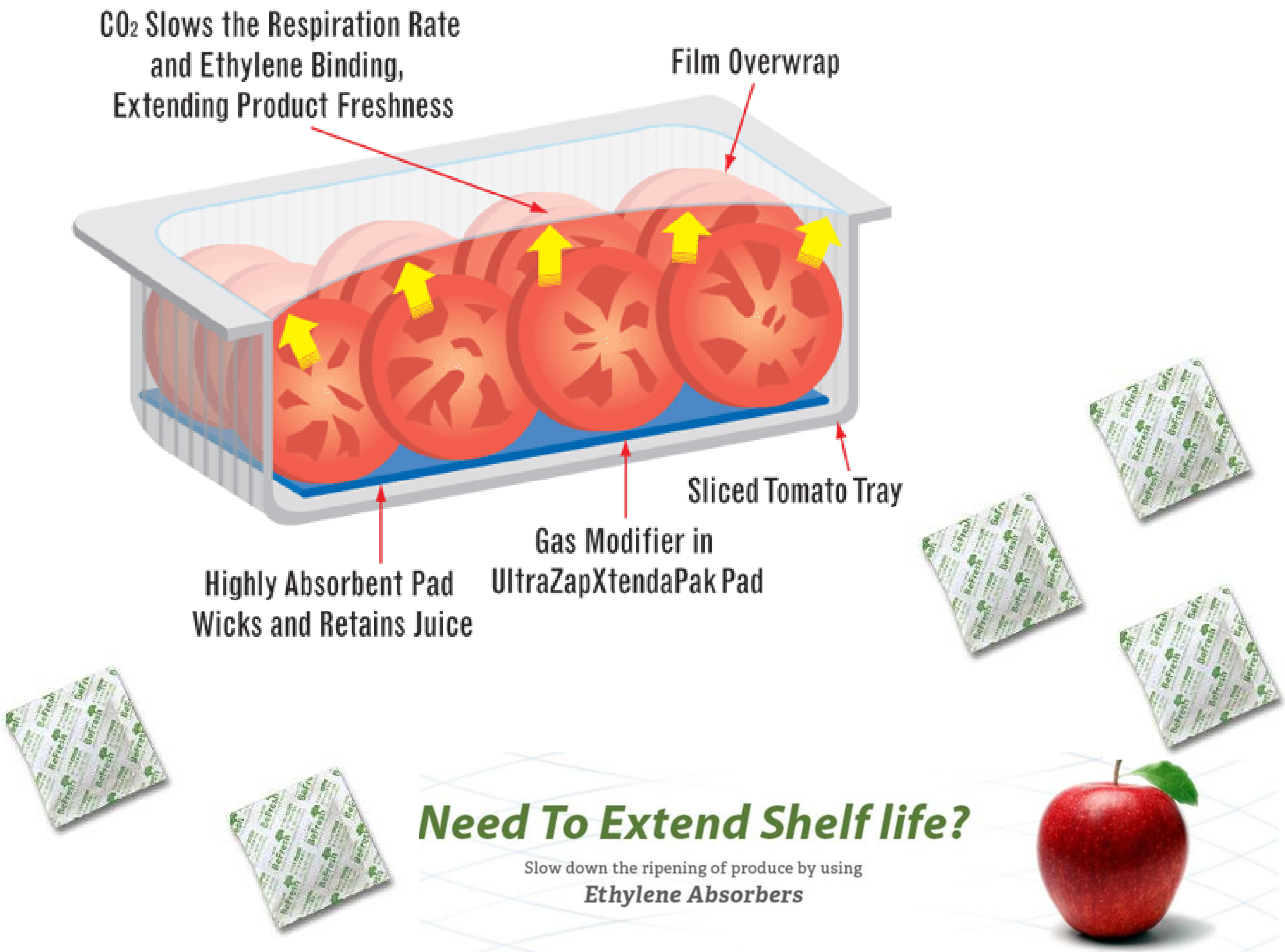



FILM
HEADSPACE
PACKAGED GOODS
(eg. Foods)
TIME
HUMIDITY
FILM
HEADSPACE
PACKAGED GOODS
(eg. Foods)
MOBILE OXYGEN MOLECULE
O2BLOCK® CLAY PLATELET
REACTED O2BLOCK® PLATELET





McAirlaid's CO_2Pad


CO_2 Slows the Respiration Rate
and Ethylene Binding,
Extending Product Freshness
Film Overwrap
Sliced Tomato Tray
Gas Modifier in
UltraZapXtendaPak Pad
Highly Absorbent Pad
Wicks and Retains Juice
Need To Extend Shelf life?
Slow down the ripening of produce by using
Ethylene Absorbers


100%
bluapple
Prolongs Freshness
KEEPS FRUITS AND VEGETABLES FRESHER LONGER
ABSORBS ETHYLENE GAS WHICH CAUSES PRODUCE TO OVER RIPEN
PAYS FOR ITSELF WEEK AFTER WEEK!
Easy to use! Place in your crisper or wherever you keep produce.
Log on to www.thebluapple.com to receive automatic email alerts when it's time to change your Bluapple™ packet.
bluapple
One Year Refill Kit
12-months of refill packets for 2 Bluapples
KEEPS FRUITS AND VEGETABLES FRESHER LONGER
ABSORBS ETHYLENE GAS WHICH CAUSES PRODUCE TO OVER RIPEN
Saves Money
Fresher Produce
Better Taste
Preserves Nutrients

Produce affected by Ethylene Gas

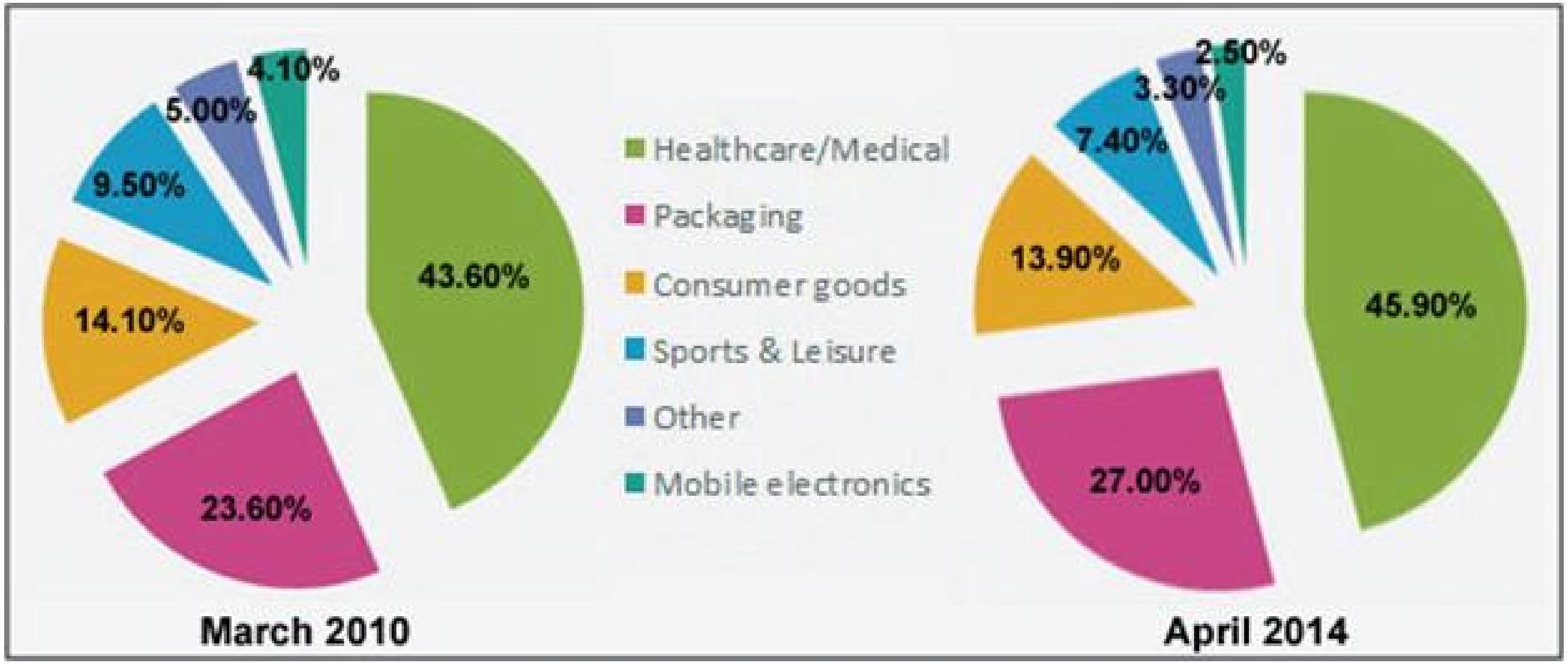
ETHYLENE-PRODUCING COMMODITIES

Apples	Dried fruit	Peaches
Apricots	Kiwifruit, ripe	Pears
Avocados	Mangoes	Plums
Cantaloupe	Papayas	Tomatoes

ETHYLENE-SENSITIVE COMMODITIES

Bananas	Cucumbers	Okra
Bell peppers	Eggplant	Peas
Broccoli	Greens	Plantains
Brussels sprouts	Green/snap beans	Spinach
Cabbage	Honeydew	Squash
Carrots	Kiwifruit, unripe	Sweet potatoes
Cauliflower	Lettuce	Watermelon

Source: *The Packer's 2005 Produce Availability & Merchandising Guide*



Market to Witness Highest Growth in Antimicrobials
Comparision of March 2010 (220 votes) & April 2014 (122 votes) Results)
Gathered from SpecialChem4Polymers Community Results of the Survey

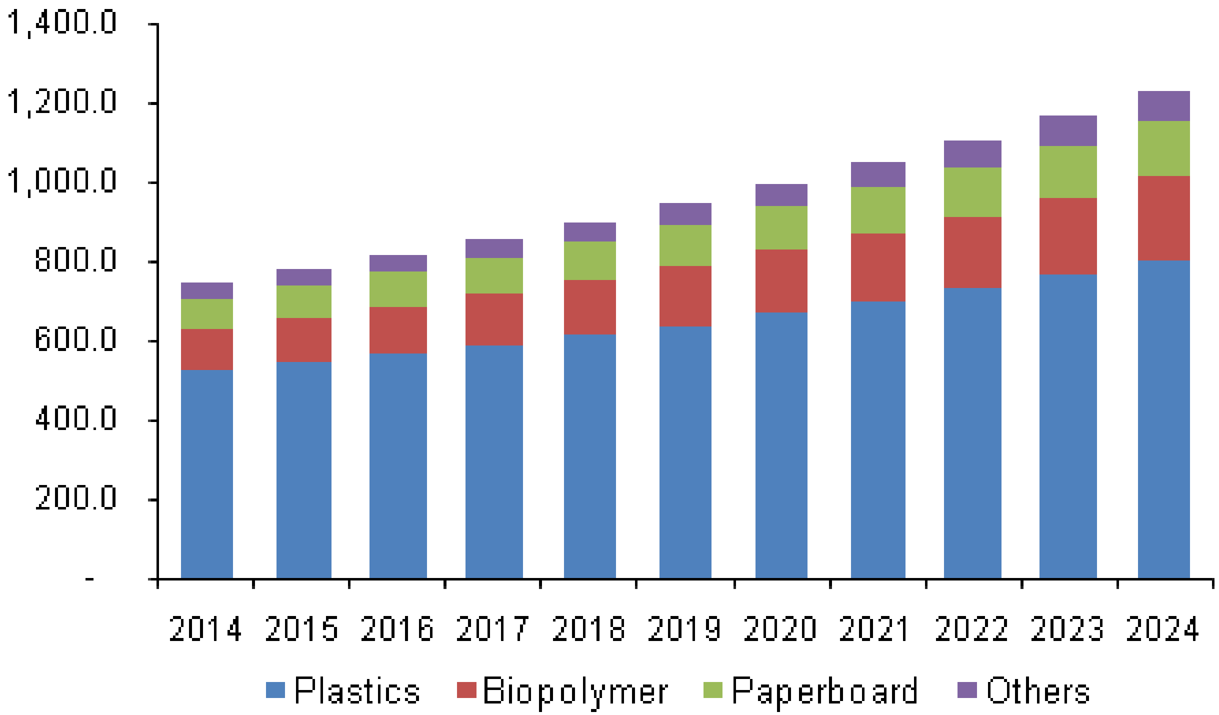
Antimicrobial packaging for food

- Micro-organisms cause spoilage of foodstuffs
- The use of traditional preservatives "inside" the food matrix is ineffective
- Microbial growth occurs mainly ***at the surface*** of solid and semisolid foodstuffs
- Antimicrobial effect can be directed at the surface of foodstuffs, for example, by using antimicrobial packaging materials which come into direct contact with foodstuffs

THE AMOUNT OF TRADITIONAL PRESERVATIVES CAN BE DECREASED

The global antimicrobial packaging market was valued at 6.51 billion € in 2015.

U.S antimicrobial packaging market volume by base material, 2012 - 2024 (Kilo Tons)



GRAND VIEW RESEARCH

Table 3. Antimicrobial substances of potential use in food packaging [31].

Type of substance	Example of substance
Organic acids	Propionic, sorbic, acetic, lactic, benzoic acid
Bacteriocins	Nisin, pediocins
Essential oils	Thymol, eugenol, cinnamic acid
Natural phenols	*p*-Cresol, hydroquinones, catechins
Enzymes	Lactoperoxidase, lysozyme, lactoferrin
Proteins	Conalbumin, cathepsin
Antioxidant phenolics	BHT (butylated hydroxytoluene), BHA
Isothiocyanates	Allylisothiocyanate, hypothiocyanite
Antibiotics	Natamycin
Antimicrobial peptides	Defensins, cecropins, attacins, magainins
Fungicides	Imazalil, benomyl
Chelatin agents	EDTA, pyrophosphate, citrates
Inorganics	Sulphites, sulphur dioxide
Metals	Silver, copper
Parabenes	Methyl, propylparaben

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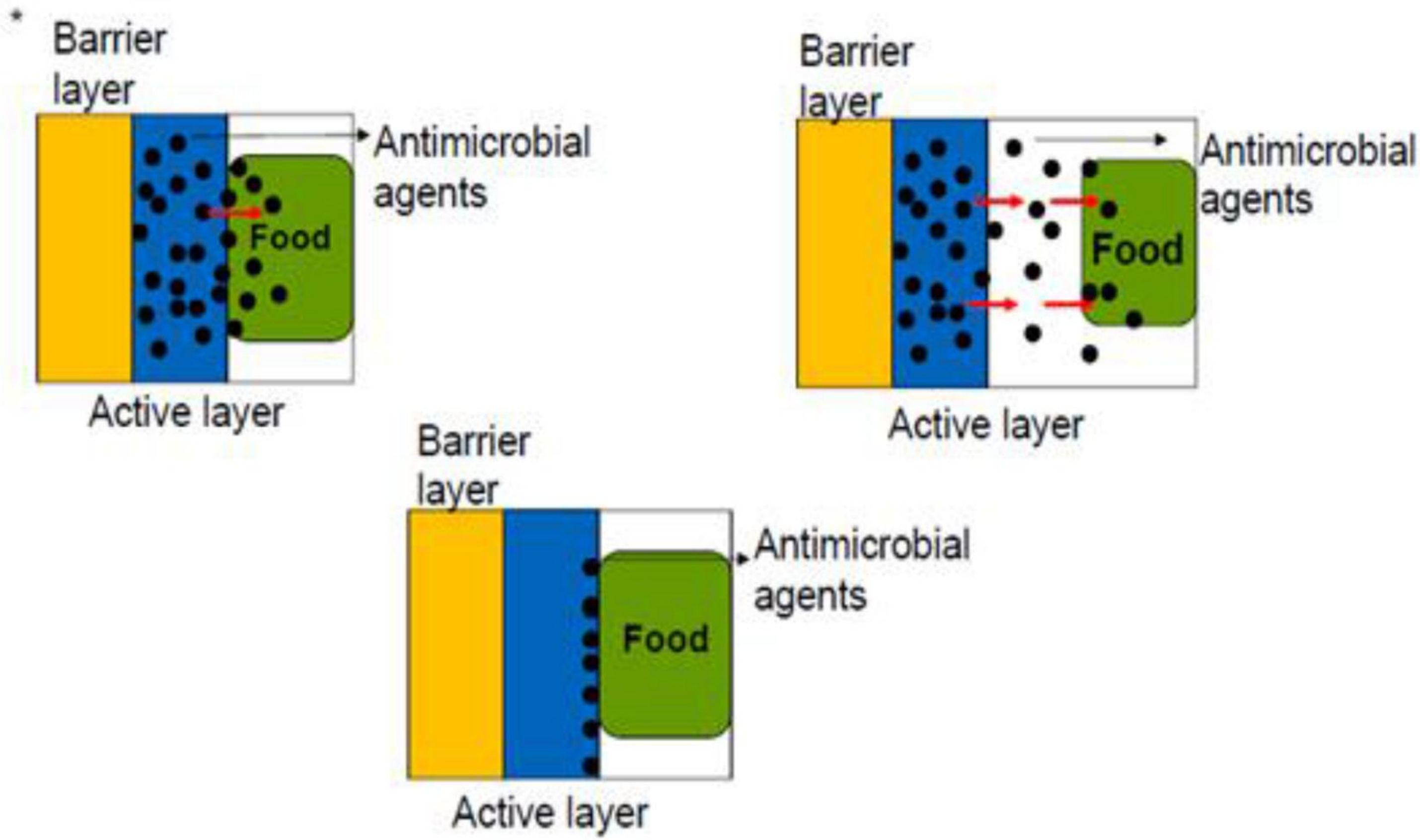

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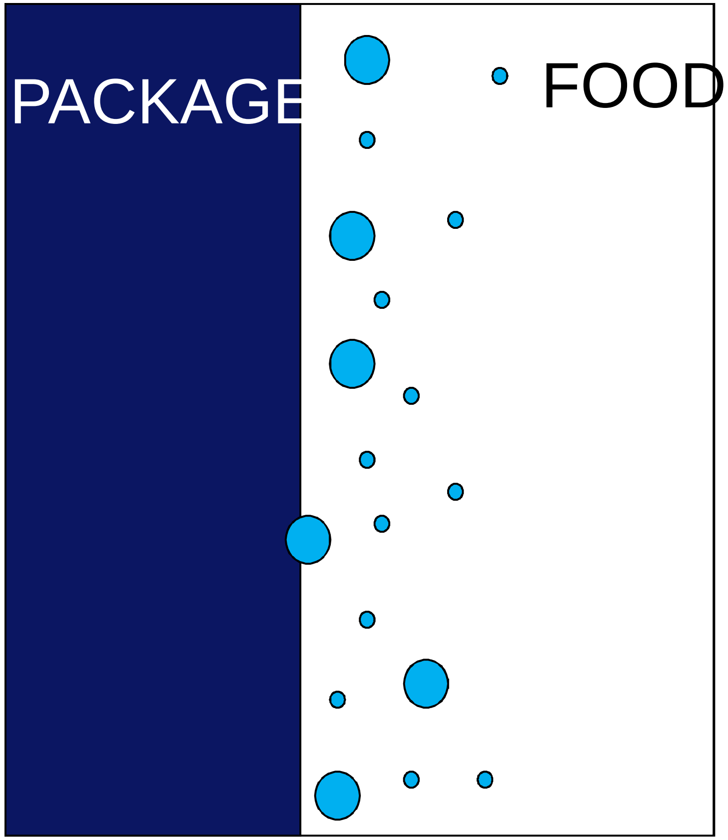
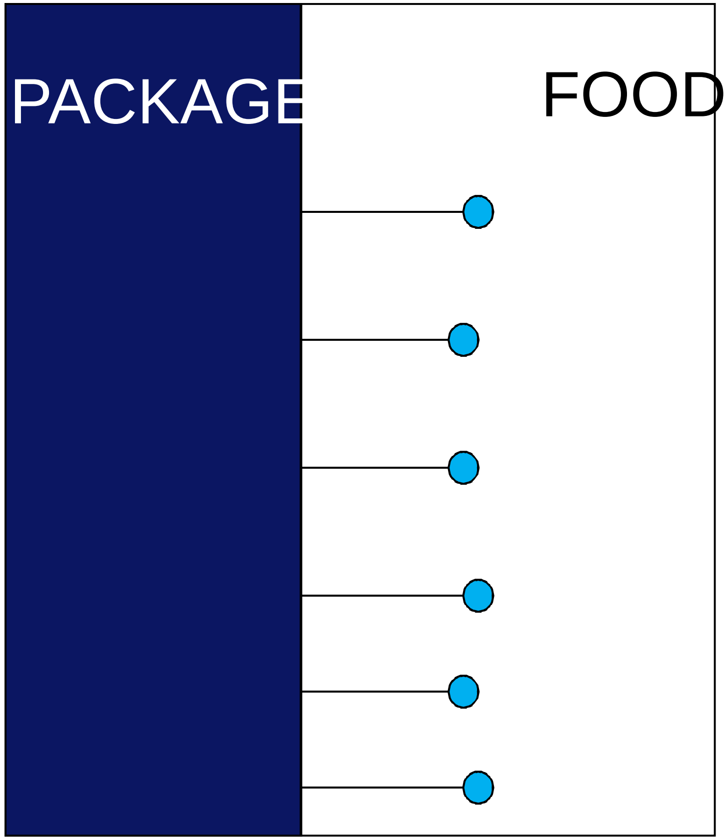


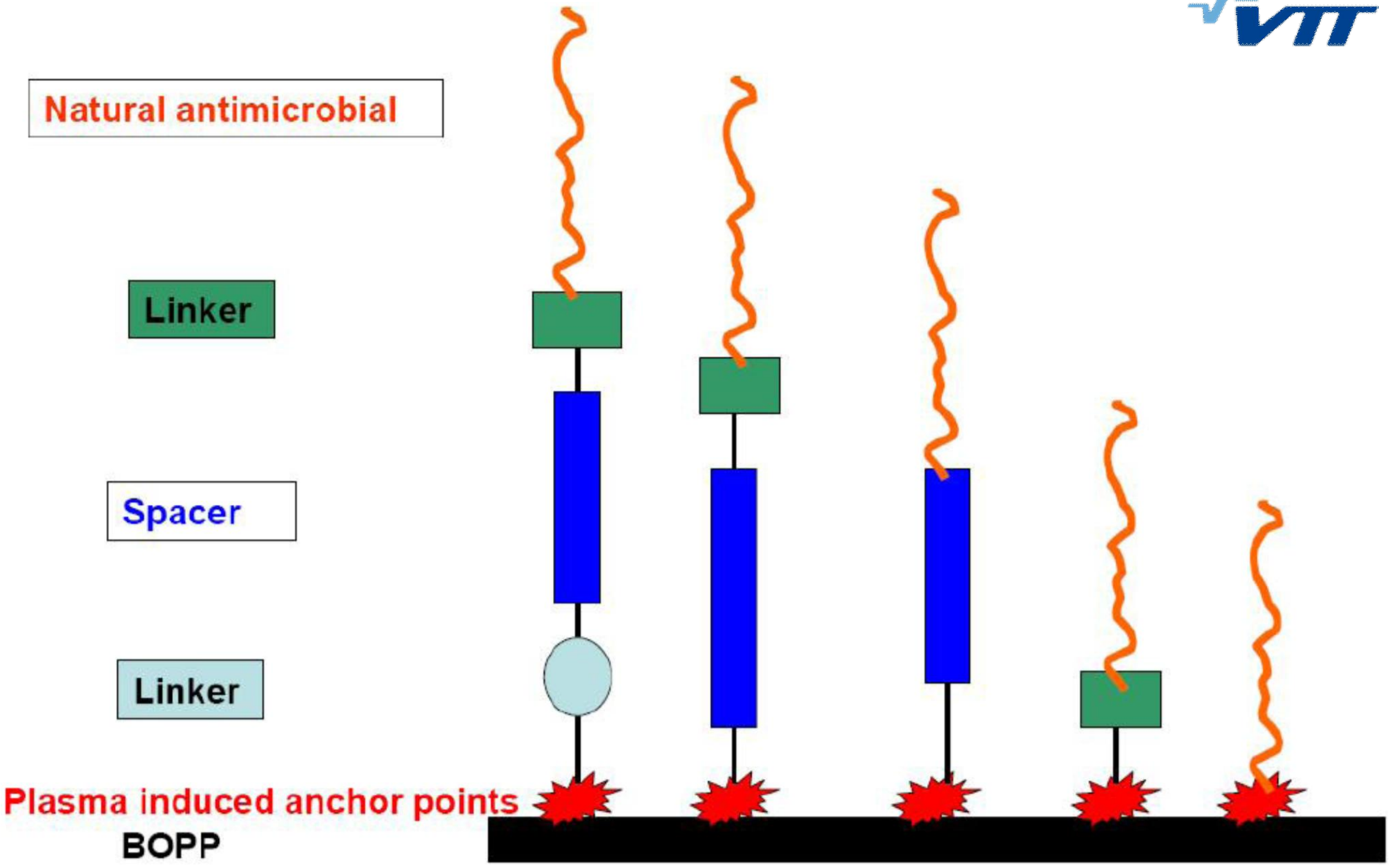
Incorporation in package

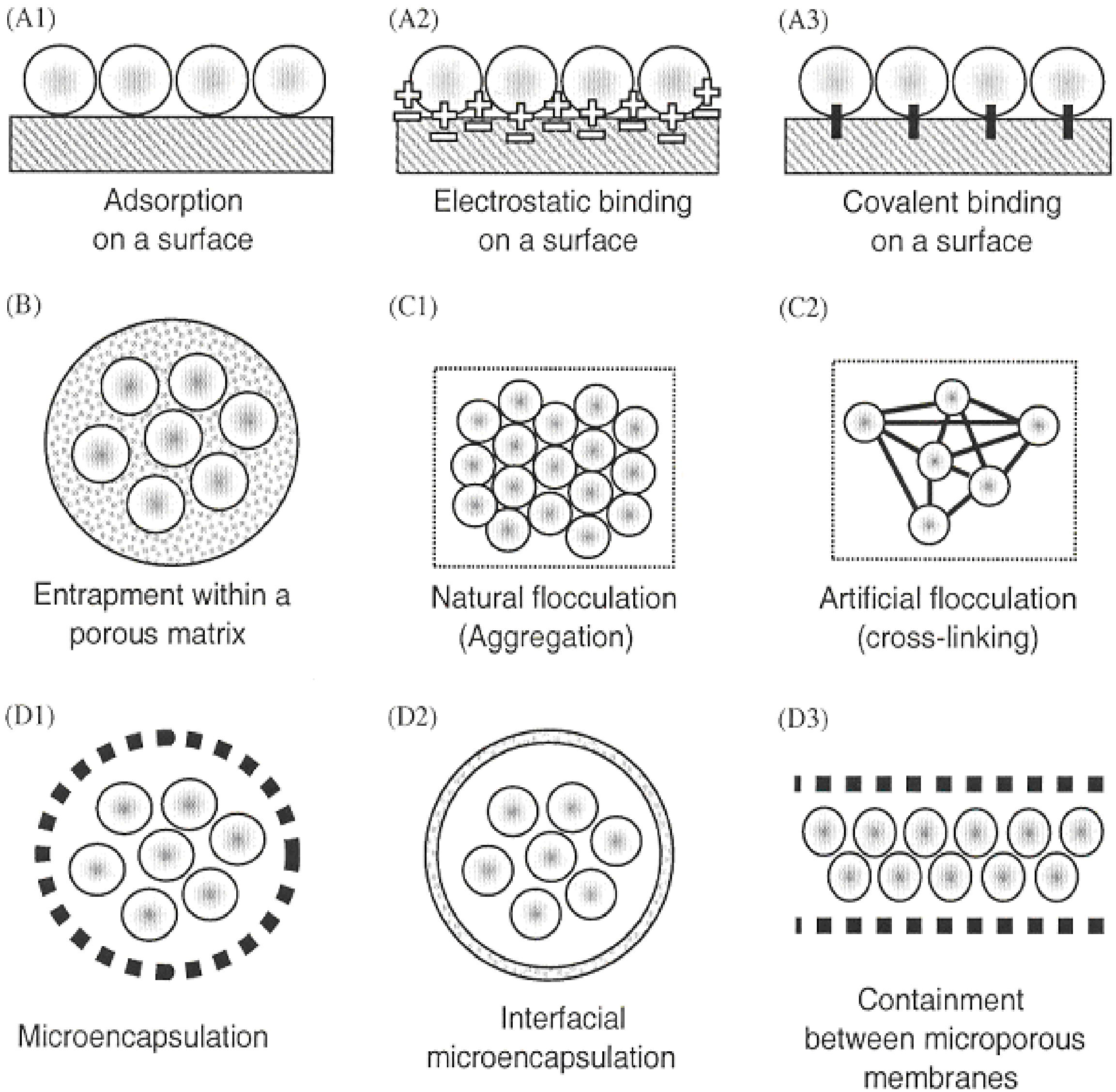


Chemical immobilization in package

Ref. Han, 2000

Immobilization principle

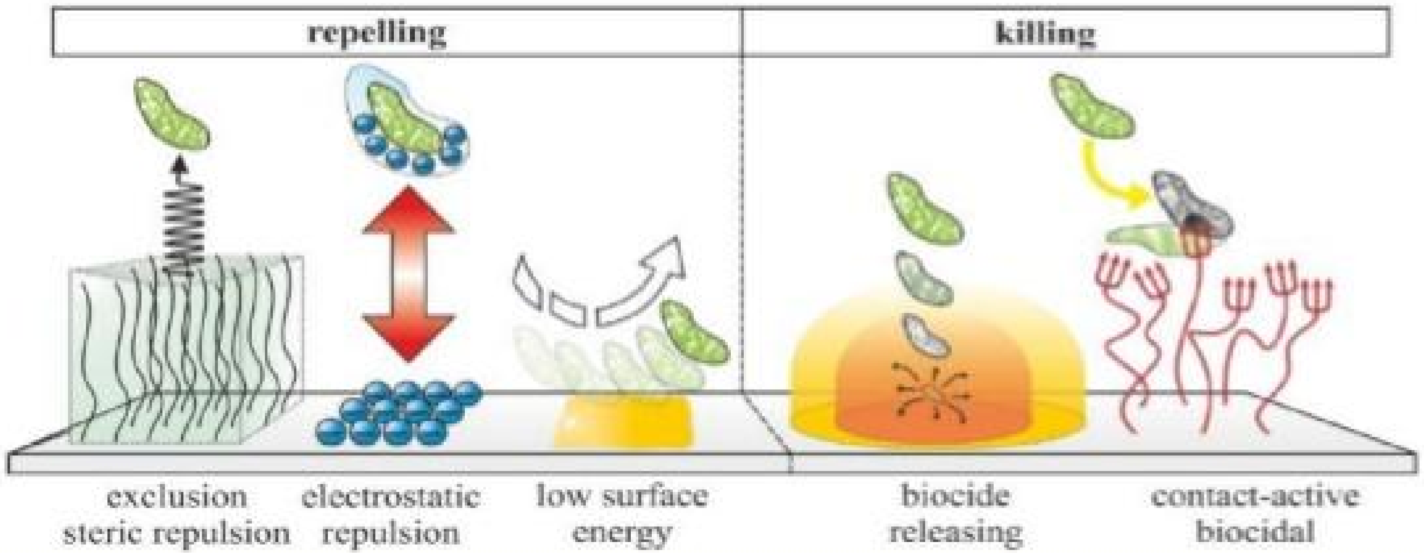



(A1)
Adsorption on a surface
(A2)
Electrostatic binding on a surface
(A3)
Covalent binding on a surface
(B)
Entrapment within a porous matrix
(C1)
Natural flocculation (Aggregation)
(C2)
Artificial flocculation (cross-linking)
(D1)
Microencapsulation
(D2)
Interfacial microencapsulation
(D3)
Containment between microporous membranes

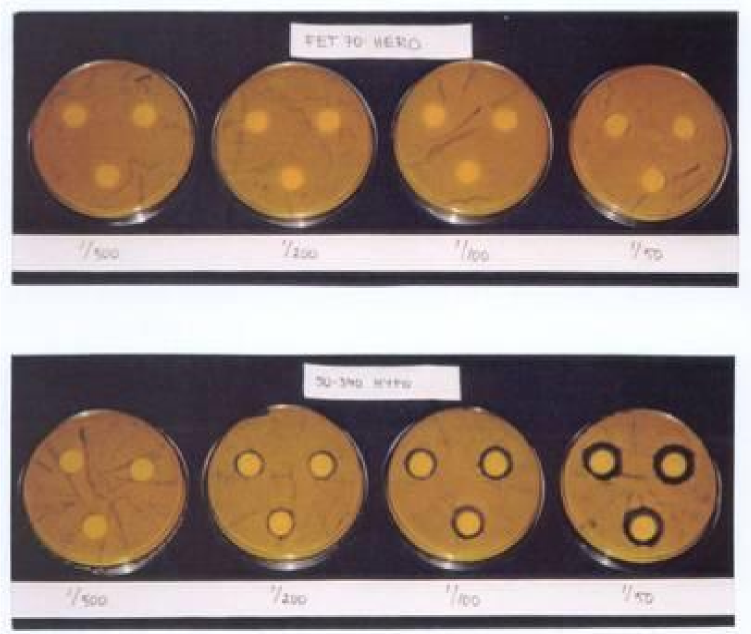
Antimicrobial packaging

The University of Queensland
Australia

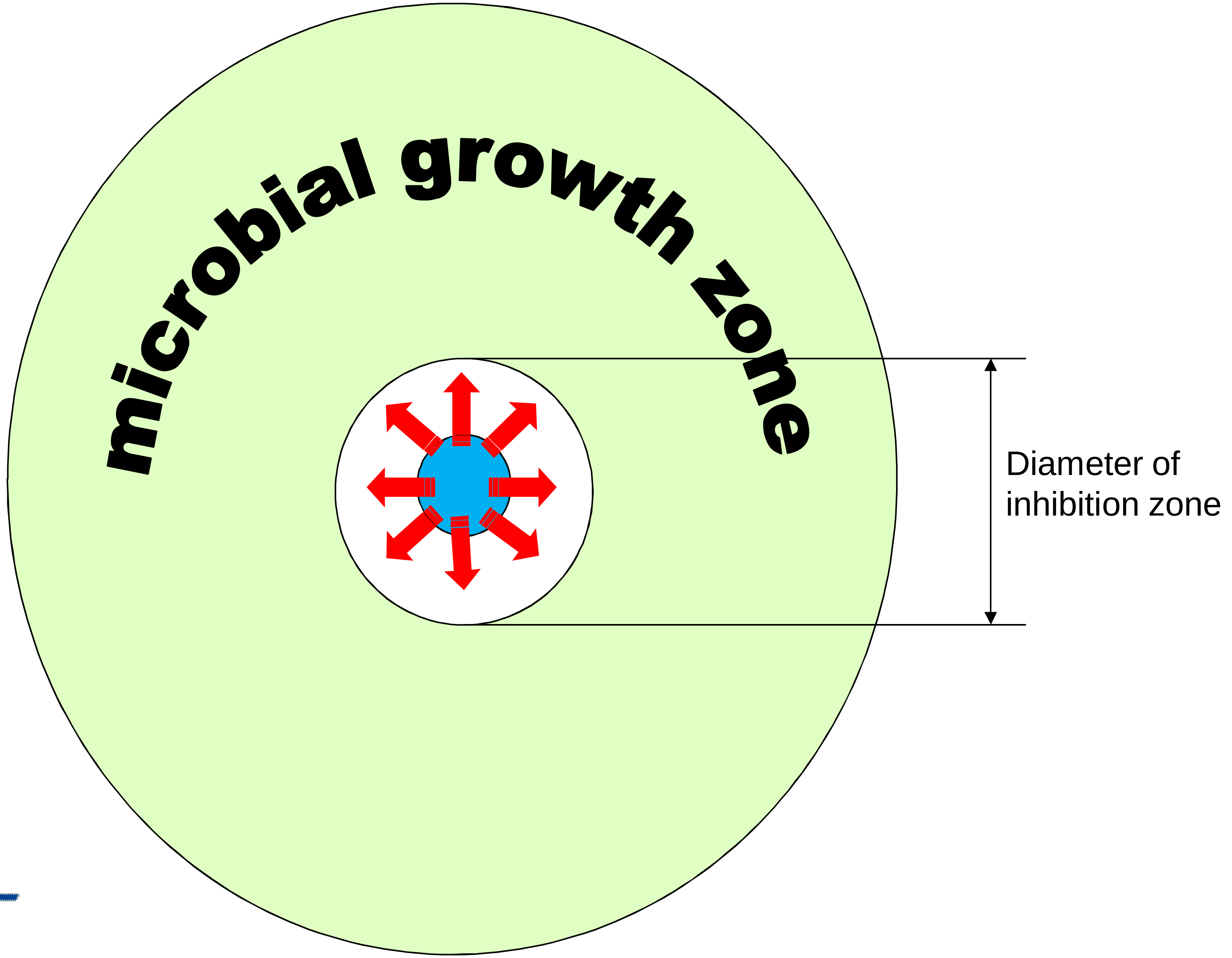
- Integration of antimicrobials agents into packaging materials
- To kill or to inhibit the pathogenic and spoilage microorganism



INHIBITION ZONE METHODS
FOR QUALITATIVE ASSESEMENT OF SURFACES WITH LEACHABLE ANTIMICROBIALS



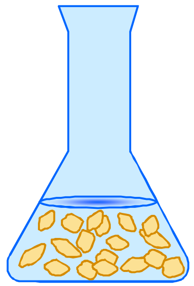
- The sample is placed on solid medium containing the test microorganism and incubated until growth is visible.
- A clear zone surrounding the sample indicates antimicrobial diffusion from the sample and subsequent growth inhibition.

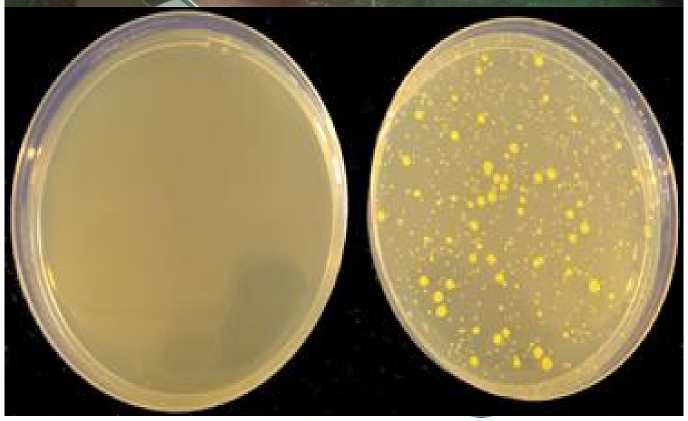

microbial growth zone
Diameter of inhibition zone

VIABLE COUNT METHODS

ASTM E2149 "Shake-flask test"

- The samples are cut to test pieces.
- The test pieces are incubated in a shake flask in bacterial suspension containing known number of test bacteria.
- After incubation the number of viable bacteria in the suspension is measured by plating
- The number of viable bacteria in the flask containing the antimicrobial sample is compared to that in the flask containing the non-treated reference.





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Antimicrobial substance	Packaging material	Target microbe	Food product	Reference
Sodium benzoate Potassium sorbate Nisin + EDTA Imazalil	Caseinate films Chitosan films Keratin films	*B. subtilis* *A. niger*	-	[173]
Sorbic acid Tocopherol Citric acid	Casein films Carnauba wax films Gelatin films Pectinate, pectate, zein films	*S. rouxii, A. niger* - -	Papaya and apricot cubes Margarine Nuts	[174]
Mustard oil	Paper/ plastic bag	*Penicillium spp., A. flavus, Endomyces fibuliger*	Rye and wheat bread	[120]
Chitosan	Chitosan coating	*S. aureus, L. monocytogenes, P. aeruginosa*	Cheese	[175]
Chitosan	Chitosan coating	*L. innocua, L. monocytogenes*	Emmental cheese	[176]
Chitosan	Chitosan coating	*Alternaria sp, Penicillium sp, Cladosporium sp.*	Precooked pizza	[177]
Chitosan	Chitosan coatings and films	*A. niger*	-	[95]
Lysozyme	Chitosan films	*S. faecalis, E. coli*	-	[96]

Benzoic acid	Methylcellulose coatings	*Zygosaccharomyces rouxii, Zygosaccharomyces mellis*	Fruit preserves	[178]
Benzoic acid Sorbic acid	Methylcellulose coatings Methylcellulose/ chitosan coatings	*P. notatum, Rhodotorula*	-	[81]
Nisin	Methylcellulose coatings Hydropropyl methylcellulose coatings	*M. luteus*	-	[179]
Potassium sorbate Acetic acid	Hydropropyl methylcellulose films	Salmonella	Tomatoes	[180]
Nisin	Hydropropyl methylcellulose films	*L. innocua, S. aureus*	-	[60]
Pediocin	Cellulose casings Plastic barrier bags	*L. monocytogenes*	Turkey breast (fresh poultry), ham (processed meat), beef (fresh meat)	[181]
Potassium sorbate	Starch films	*E. coli,* salmonella	Chicken breast	[182]
Lactic acid	Alginate films	*E. coli,* salmonella, *L. monocytogenes*	Lean beef muscle	[183]

Glucose oxidase	Alginate films	-	Fish	[184]
p-Aminobenzoic acid Potassium sorbate Acetic acid Lactic acid	Whey protein based (WPI) films	*L. monocytogenes, E. coli,* salmonella	Bologna slices Sausage slices Hot dogs	[185-187]
Nisin	Whey protein based (WPI) films	*L. monocytogenes*	-	[188]
Nisin + EDTA Lysozyme + EDTA Propyl paraben	Whey protein based (WPI) films	*B. thermosphacta,* salmonella, *E. coli, L. monocytogenes, S. aureus*	-	[188-189]
Nisin Lysozyme + EDTA	Soy protein isolate films Corn zein films	*L. plantarum, E. coli*	- -	[57]
Nisin	Corn zein films	*L. monocytogenes*	Milk	[190]
Nisin	Corn zein films	*L. monocytogenes*	Chicken	[191]
Potassium sorbate	Corn zein films	*S. aureus*	Cheese	[46]
Sorbic acid	Corn zein films Wheat gluten films	*L. monocytogenes*	Cooked sweet corn	[192]
Nisin (adsorbed)	LDPE films	*L. monocytogenes*	-	[68]
Acetic acid Propionic acid Lauric acid Cinnamaldehyde	Chitosan films	Enterobacteriaceae, *Lactobacillus sakei, Serratia liquefaciens*	Bologna, cooked ham, pastrami	[193]
Allyl-isothiocyanate	Labels	Moulds	Lettuce, turnip greens, fresh ground mince, kiwifruit, strawberries, rock cake, bread rolls	[194]

Silver	Plastics	-	Cheese	[195]
Nisin Tocopherol	Vinyl acetate-ethylene copolymer binder (Elvace) on paper	*M. flavus*	-	[38]
Nisin Sorbic acid Potassium sorbate	PVDC films	*L. monocytogenes*	-	[53]
Benzoic anhydride	LDPE films	*Rhizopus stolonifer, Penicillium spp., A. toxicarius*	Cheese	[72]
Benzoic acid Sorbic acid	Poly(ethylene-co-methacrylic acid) PEMA	*Penicillium spp., A. niger*	-	[73]
Grapefruit seed extract	LDPE films	*S. aureus, E. coli*	Curled lettuce, Soybean sprouts	[196]
Potassium sorbate	LDPE films	Yeasts	-	[54]
Nisin Citric acid Lactic acid Malic acid Tartaric acid	Soy protein films	*L. monocytogenes, E. coli,* salmonella	-	[197]
Hexamethylenetetramine	LDPE films	Yeasts, lactic acid bacteria	Orange juice, Cooked ham	[44]
Benzoic anhydride	LDPE films	-	Cheese, Toasted bread	[32]
Nisin (adsorbed)	PVC films LLDPE films Nylon films	Salmonella	Broiler	[65]

Nisin, Lacticin from *Lactococcus lactis*	Polyamide coatings on LDPE films	Total aerobic bacteria, coliform bacteria	Fresh oyster, Ground beef	[198]
Benzoic acid Benzoyl chloride	Ionomer films	*Penicillium spp., A. niger*	-	[199] [296]
Nisin (adsorbed)	Plastic film (70:30, PE:PA)	*L. innocua, S. aureus*	Sliced cheese and ham	[170, 200]
	Greaseproof and moisture resistant packaging papers	*L. innocua, S. aureus*	-	
Imazalil	Vinyl acetate copolymer coatings	Molds, *Penicillium echinulatum*	Hard and semi-hard cheeses	[123]
Silicon quaternary ammonium salt	Adhesive layer on plastic film (Cryovac D-955)	*Helminthosporium solani*	Potatoes	[127]
Extracts (*Rheum palmatum, Coptis chinensis*) Ag-substituted zirconium Sorbic acid	LDPE films	- - *E. coli, S. aureus, Leuconostoc mesenteroides*	Fresh curled lettuce cucumber	[114]
Basil (linalool, methyl chavicol)	LDPE films	*E. coli, L. innocua*	Cheddar cheese	[115,317, 324]
Nisin	Sorghum starch and flour films	*Lactobacillus delbrueckii*	-	[61]

Chitosan	Chitosan coatings	Fungi	Clementine mandarin fruit	[203]
Chitosan Lactic acid/ sodium lactate	Chitosan coatings	Total aerobic psychrotrophic bacteria, lactic acid bacteria, yeast	Strawberry Lettuce	[204]
Nisin	Wheat gluten films	*L. monocytogenes*	Turkey bologna	[70]
Lysozyme Nisin Sodium benzoate	PVOH films	*M. luteus, Alicyclobacillus acidoterrestris, S. cerevisiae*	-	[37,150]
Chitosan	Yam starch films	Salmonella	-	[205]
Herbs (oregano, marjoram, thyme)	Plastic film	-	Hamburger meat patties, pizza	[206]
Essential oils (oregano, pimento)	Casein/ whey protein isolate films	*E. coli, Pseudomones spp.*	Beef muscle	[116]
Nisin	Hydroxypropylmet hylcellulose films	*M. luteus*	-	[207]
Potassium sorbate Sorbic acid	Celluse-based coating	Salmonella	Eggs	[208]
Benzoic acid Sorbic acid	Varnish on plastic films	-	Fresh meat and cheese	[209]
Allyl-isothiocyanate, imazalil	Cyclodextrin + PLA and PLA/PCL films	*Penicillium commune, P. roqueforti, P. nalgiovense, P. verrucosum, P. caseifulvum, P. camemberti and K. maxianus*	Cheese	[210]

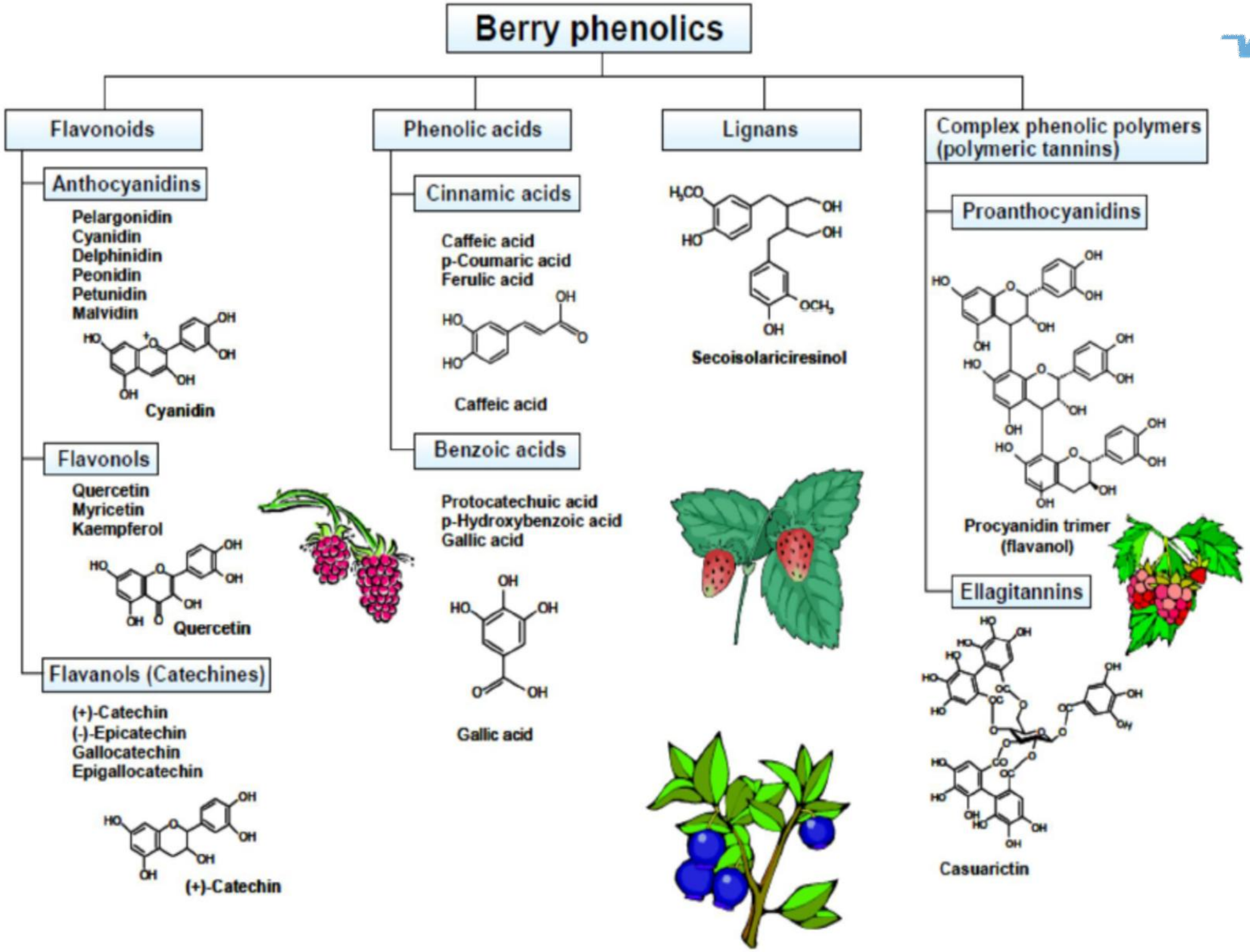
Butylhydroxytoluene (BHT)	HDPE films	-	Fresh oat flaked cereal	[211]
Sorbic acid	Butter paper	Bacteria, yeasts, molds	*Paneer* from milk	[55]
Lysozyme	PVOH, nylon, cellulose triacetate (CTA) films	*M. luteus*	-	[148]
Propyl paraben	Styrene-acrylate copolymer coating on paper	*S. cerevisiae*	-	[33]
Potassium sorbate Citric acid	Starch-based coatings	Bacteria, molds and yeasts	Strawberry	[212]
Calcium sorbate	CMC/ paper	-	Bread	[213-214]
Benomyl	Ionomer films	Fungi	-	[172]
Imazalil	LDPE films	-	Bell pepper	[124]
Imazalil	LDPE films	Molds	Cheese	[122]
Ethanol vapour	Silicon oxide sachet (Ethicap)	-	Bakery	[215]
Iodine potassium iodide, Sodium ortho-phenylphenate, Biphenyl, Diphenylamine, Dichloronitroaniline	Paper wraps	*Trichothecium roseum, Glomerella cingulata, Penicillium expansum, Rhizopus stolonifer*	Golden Delicious apples	[216]
Chitosan	BOPP films	*E. coli, B. subtilis*	-	[217]
Glucose oxidase	BOPP films	*E. coli, B. subtilis*	-	[218]
Lactic acid	Chitosan coated paper	*B. subtilis*	-	[219]

Sodium benzoate Potassium sorbate Sodium nitrite Sodium lactate	LDPE films PS PET Poly(maleic acid-co-olefine)	*B. subtilis, A. niger*	-	[220]
Nisin	Cellulose casings	*L. monocytogenes*	Frankfurters	[221]
Lysozyme EDTA	Corn zein films	*B. subtilis,* *L. plantarum, E. coli*	-	[71]
Lactoperoxidase system	Whey protein films and coatings	*L. monocytogenes*	Smoked salmon	[222]
Lactoperoxidase system	Whey protein films and coatings	Salmonella, *E. coli,* *P. commune*	Roasted turkey	[223,224, 300]
Cinnamon	PET container	*Moulds*	Marmelade	[225]
Nisin	Methylcellulose and hydroxypropyl methylcellulose coatings on LDPE	*L. monocytogenes*	-	[68]
Silver	Polyethyleneoxide coating on PE films	*Alicyclobacillus acidoterrestis*	Apple juice	[226]
Sodium propionate Sodium sorbate Sodium benzoate Nisin	Acrylic polymer or vinyl acetate-ethylene copolymer binder on paper	*M. flavus*	-	[35]
Imazalil EDTA	LDPE films	*B. subtilis, A. niger*	-	[227]
Nisin	LDPE films	*M. luteus*	Milk	[266]
TiO_2	PP films	*Penicillium expansum*	Lemon fruit	[271]

$SO_2 + CO_2$	Cardboard box	*Botrytis cinerea*	Grape fruit	[272]
Sorbic anhydride	PE films	*A. niger, Penicillium sp.*	-	[276]
Lysozyme, nisin, grape fruit seed extract (GFSE), EDTA	Na-alginate, κ-carrageenan-based films	*M. luteus*, listeria, salmonella, *E. coli, S. aureus*	-	[277]
Nisin	PE/biopolymer (methylcellulose, hydroxypropyl methylcellulose, κ-carrageenan or chitosan)	*M. luteus*	-	[278]
Garlic oil, potassium sorbate, nisin	Chitosan films	*S. aureus, L. monocytogenes, B. cereus*	-	[281]
Nisin Chitosan	Vinyl acetate ethylene co-polymer coating on paperboard	Aerobic bacteria and yeasts	Pasteurized milk and orange juice	[284]
Lysozyme	Whey protein isolate (WPI) films and coatings	*L. monocytogenes*	Cold-smoked salmon	[286]
Nisin + grape seed extract (GSE) green tea extract (GTE)	Soy protein films and coatings	*L. monocytogenes*	Turkey frankfurters	[287]
Bacteriocin from *Lactobasillus curvatus* (adsorbed)	PE films	*L. monocytogenes*	Pork steak, ground beef	[288]
Trans-cinnamaldehyde + e-beam irradiation	Polyamide coating on LDPE films	*L. innocua*	Fresh-cut romaine lettuce	[292]

Chlorine dioxide Allyl isothiocyanate	Sachets in multilayer barrier tray	*L. monocytogenes,* salmonella	Chicken breast	[303]
2E-hexenal	Cyclodextrin + PLA	Fungi	Blueberries	[306]
Ion-exchanged zeolite	PE film	*E. coli*, salmonella, *S. typhimurium*	Iceberg lettuce	[307]
Lysozyme	Chitosan films	*L. monocytogenes, E. coli, P. fluorescens,* molds, yeasts	Mozzarella cheese	[311]
Antimicrobial peptide dermaseptin K_4K_{20}-S4	Starch coating on PE films	Molds, aerobic bacteria	Fresh cucumber	[314]
Natamycin	Celluse-based film	*Penicillium roqueforti*	Gorgonzola cheese	[315]
Enterocins	Alginate, zein and PVA films	*L. monocytogenes*	Sliced cooked ham	[320,321]
Nisin, sodium lactate, sodium diacetate, potassium sorbate, sodium benzoate	Chitosan coatings on Surlyn film	*L. monocytogenes*	Ham steaks	[325]
Allyl isothiocyanate	Labels in packaging	*P. commune, P. roqueforti, A. flavus*	Cheese	[327]
Sorbic acid	Cellulose polymer film	Mesophilic and psychotropic bacteria, *Staphylococcus* spp.	Pastry dough	[330]
2-nonanone	PP/EVOH cups	*Botrytis cinerea*	Strawberries	[331]
Cinnamaldehyde – enriched cinnamon essential oil	Paraffin coated paper	Fungi	Strawberries	[333]
Oregano	PE film	*Yersinia enterocolitica*	Beef meat	[335]
Nisin	PP/PA/PP interleavers	Salmonella	Cooked ham	[345]

Natural antimicrobial and antioxidant compounds



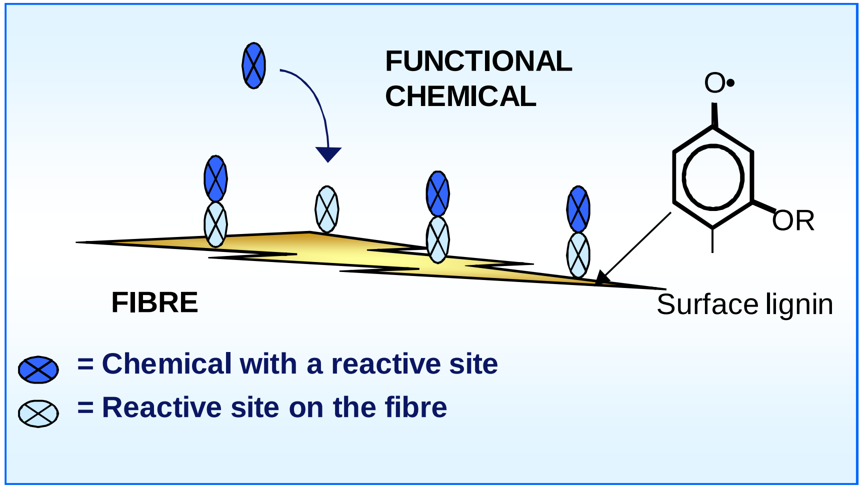
Chemo-enzymatic functionalisation of lignin-containing fibre materials

PRINCIPLE OF THE METHOD

- Based on laccase-catalysed oxidation of phenolic -OH to phenoxy radicals
- Activation + Bonding = Functionalisation
- Functional chemicals selected based on target modification

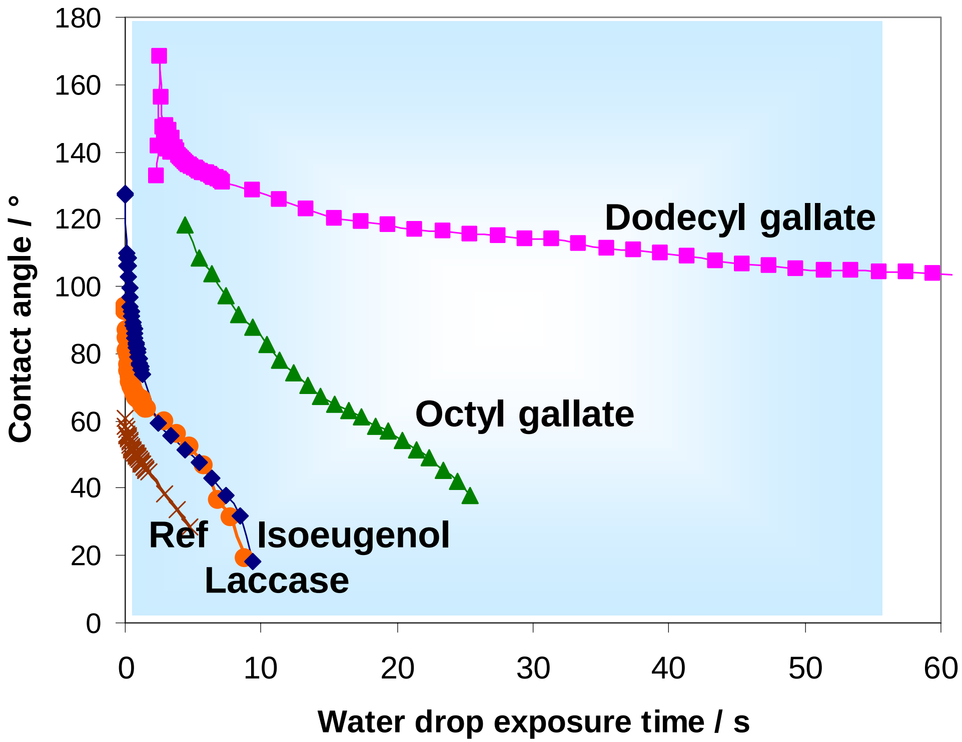
FUNCTIONAL PROPERTIES ADDED TO FIBRES:

- Charge
- Hydrofobicity
- Conductivity
- Traceability
- Antimicrobial activity

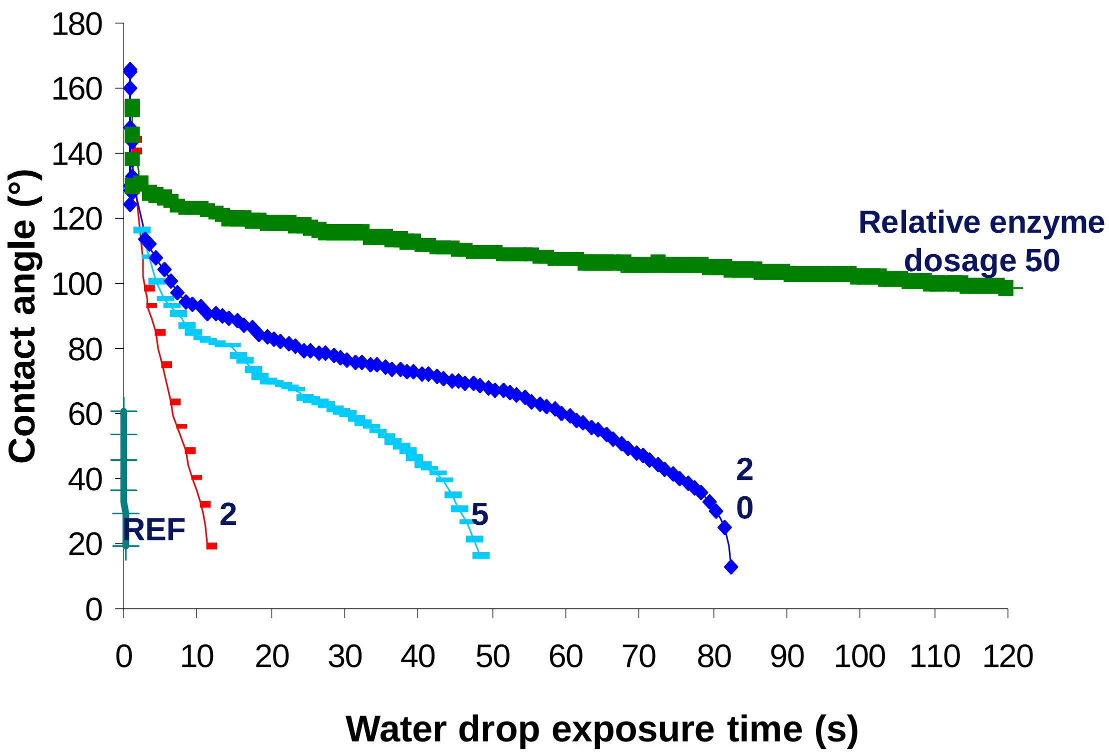


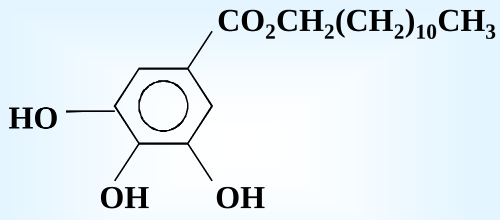
Adjusting the level of hydrophobicity

Hydrophobicity: isoeugenol < octyl gallate < dodecyl gallate



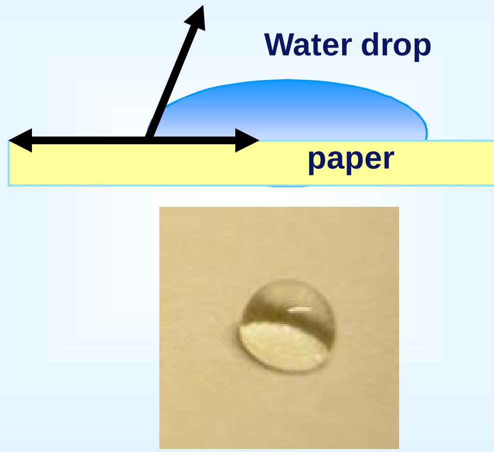
Adjusting the level of hydrophobicity



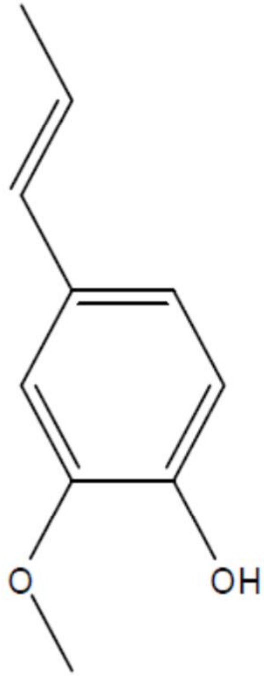


Dodecyl gallate

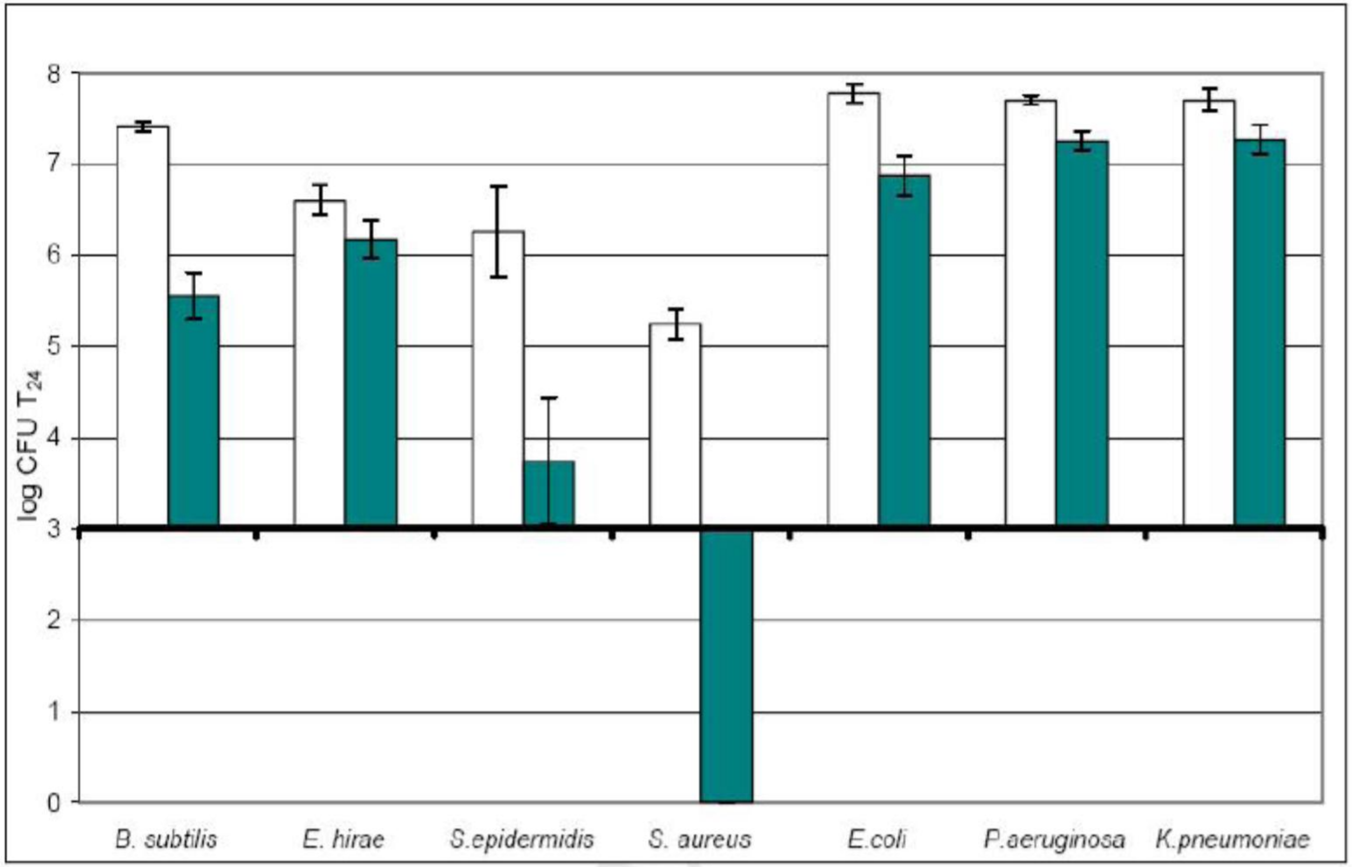
Contact angle measurement



Laccase-mediated grafting of phenolic antimicrobials



isoeugenol



Elegir et al. (2008) *Enzyme and Microbial Technology*

Antimicrobial papers

Releases the active ingredient Benzalkonium chloride when in contact with wet hands

Low-cost, compostable and infused only with organic spices, FreshPaper keeps produce fresh for 2-4x longer.

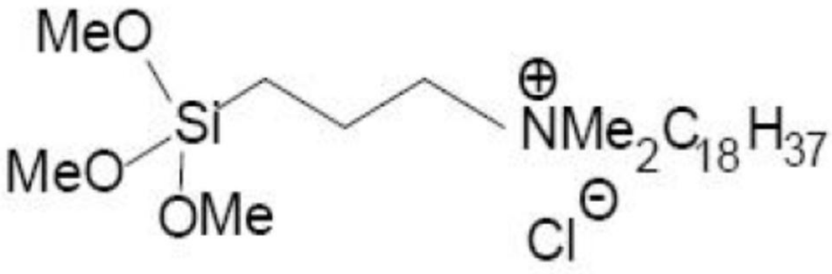
•Prevention of germ growth
•Inhibition of mould (Candida albicans)
•Hygiene maintenance and significant bacteria reduction (E.coli, S.aureus)
•Odour control
•Increase in shelf life and product freshness

Antimicrobial plasters

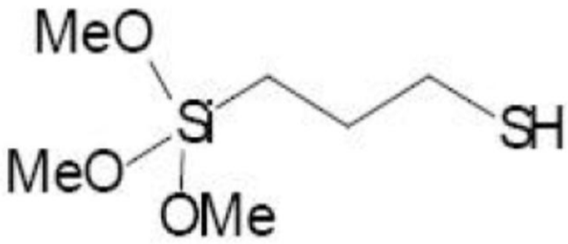
Antimicrobial bottles

Both containers and labels have proven efficacy across a broad spectrum of bacteria including MRSA and E. Coli. Both are based on ionic silver, a natural compound that kills over 99.9% of bacteria and provides food safe contact. Bottles and jars are available in SAN, PP, PET and HDPE.

Antimicrobial sol-gel precursors



Octadecylammonium-
trimethoxysilane, ODAMO



Mercaptopropyl-
trimethoxysilane
MPTMO

Antimicrobial activity of surface treated with sol-gels; ODAMO (SO154) and MPTMO (SO151)

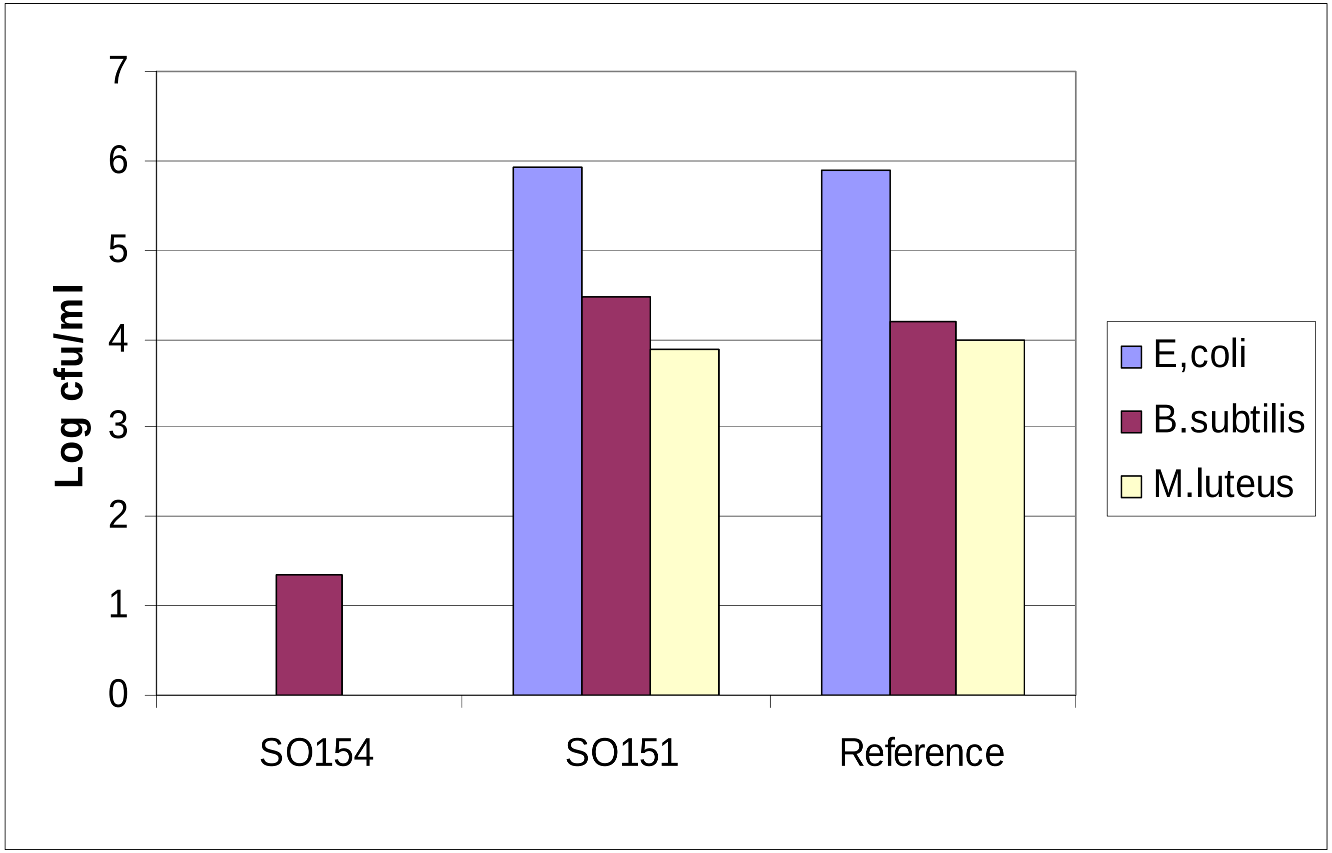


Table 1. Antimicrobial activity[a] of LDPE plates expressed as a mean diameter (mm) of inhibition zone.

Type of Plate (Thickness 2 mm)	*Bacillus subtilis* (1 day @ 30°C)	*Aspergillus niger* (2 days @ 30°C)
LDPE	–	–
LDPE + 0.05% imazalil	–	15
LDPE + 1% EDTA	–	–
LDPE + 0.025% imazalil + 0.5% EDTA	–	13
LDPE + 0.25% imazalil	–	40
LDPE + 5% EDTA	32	–
LDPE + 0.125% imazalil + 2.5% EDTA	35	19

[a]Means ($n = 3$).

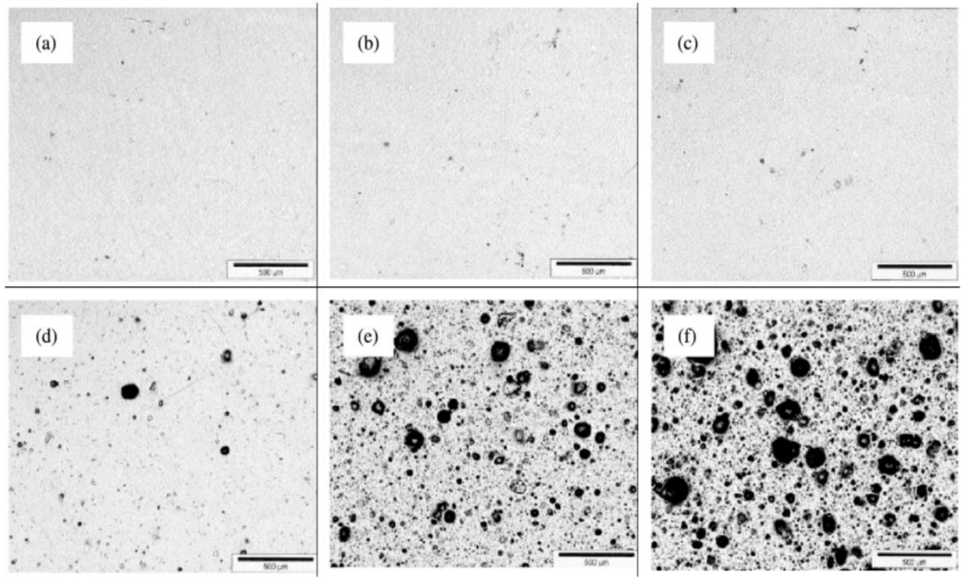


Figure 5. Structure of (a) 0.02% imazalil; (b) 0.1% imazalil; (c) 0.2% imazalil; (d) 0.5% EDTA; (e) 2.5% EDTA and (f) 5% EDTA containing LDPE films (Olympus BX 50 microscope equipped with PCO CCD IMAGING SenseCam 12 BIT COOLEDIMAGING).

Vartiainen et al. (2003) Journal of Plastic Film and Sheeting. Vol. 19 (2003) No: 4, 249 - 262

Table 1. Antimicrobial activity[a] of plastic plaques expressed as a mean diameter (mm) of inhibition zone

Type of plaque (thickness 2 mm)	*Bacillus subtilis*	*Aspergillus niger*
LDPE	–	–
LDPE + 15% sodium benzoate	26	–
LDPE + 15% potassium sorbate	16	–
LDPE + 15% sodium nitrite	44	42
LDPE + 15% sodium lactate	–	–
MA	–	–
MA + 15% sodium benzoate	30	–
MA + 15% potassium sorbate	15	–
MA + 15% sodium nitrite	44	25
MA + 15% sodium lactate	–	–
PS	–	–
PS + 15% sodium benzoate	47	–
PS + 15% potassium sorbate	23	–
PS + 15% sodium nitrite	51	32
PS + 15% sodium lactate	–	–
PET	–	–
PET + 15% sodium benzoate	48	–
PET + 15% potassium sorbate	31	–
PET + 15% sodium nitrite	65	40
PET + 15% sodium lactate	–	–

[a] Means ($n = 3$).

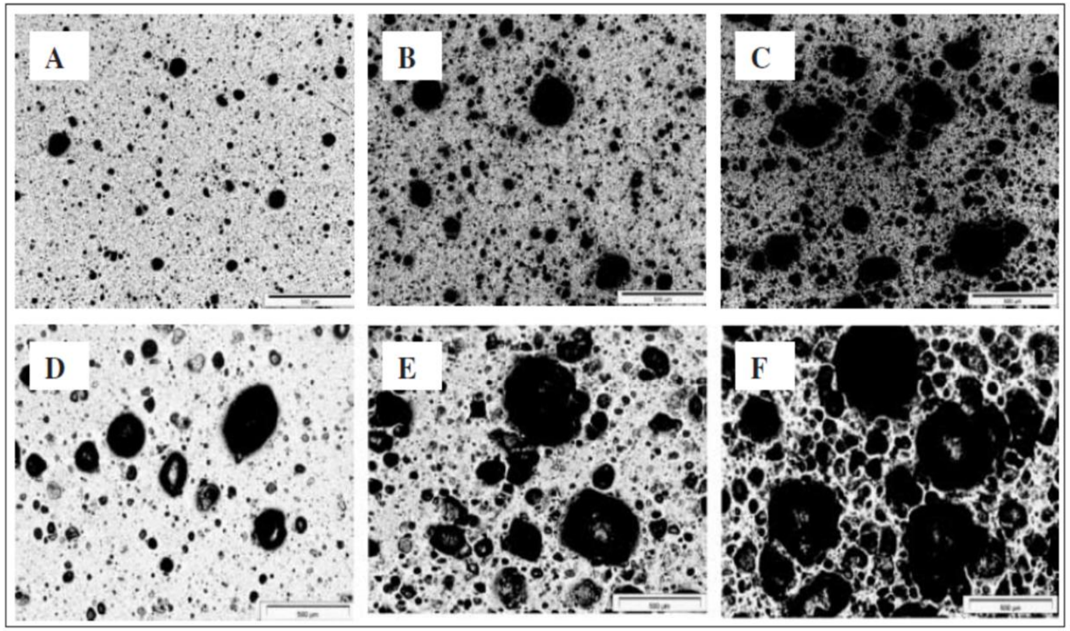
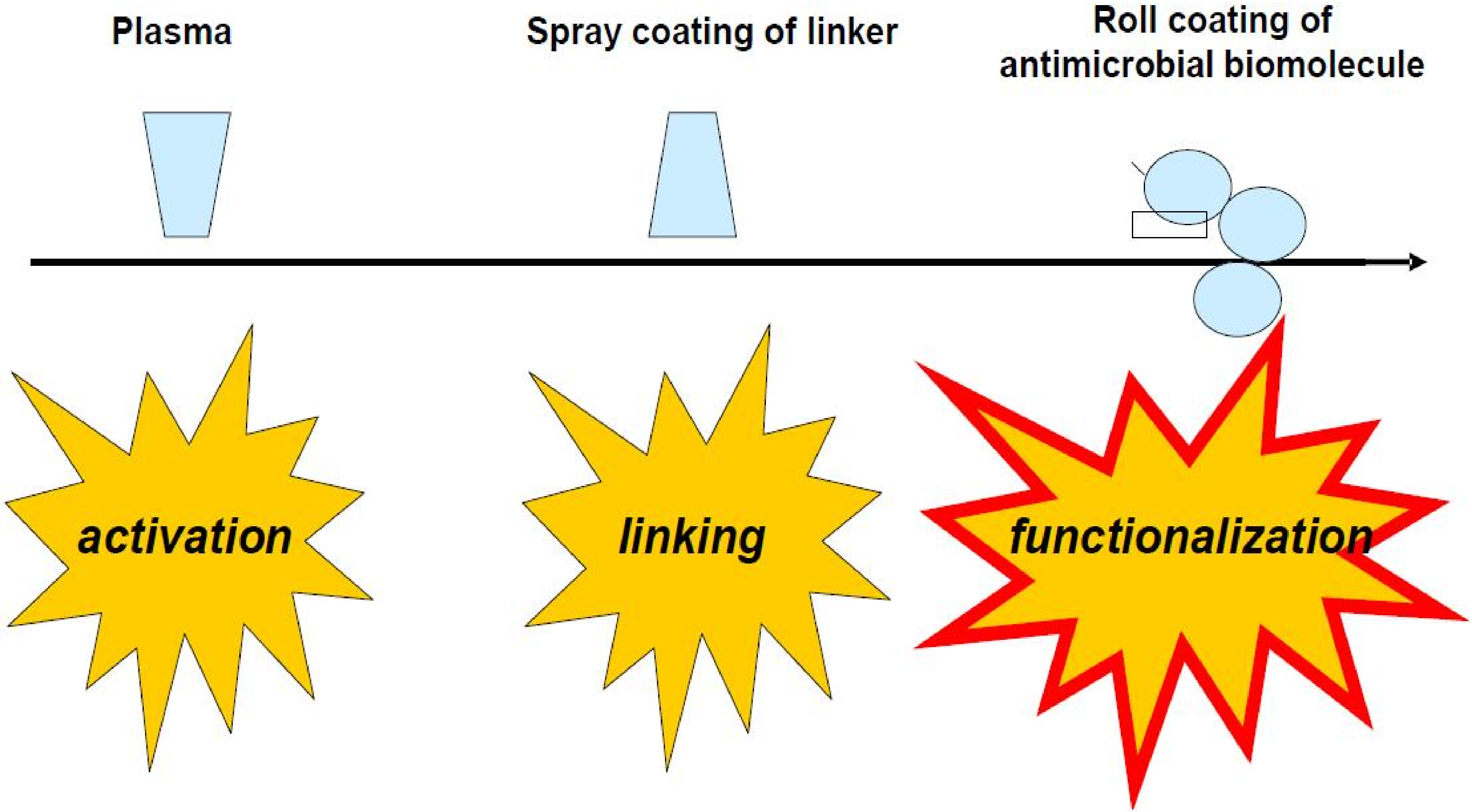


Figure 5. Structure of (a) 2.5% sodium benzoate, (b) 7.5% sodium benzoate, (c) 15% sodium benzoate, (d) 2.5% sodium nitrite, (e) 7.5% sodium nitrite and (f) 15% sodium nitrite containing LDPE films (Olympus BX 50 microscope equipped with PCO CCD IMAGING SenseCam 12 BIT COOLED IMAGING).

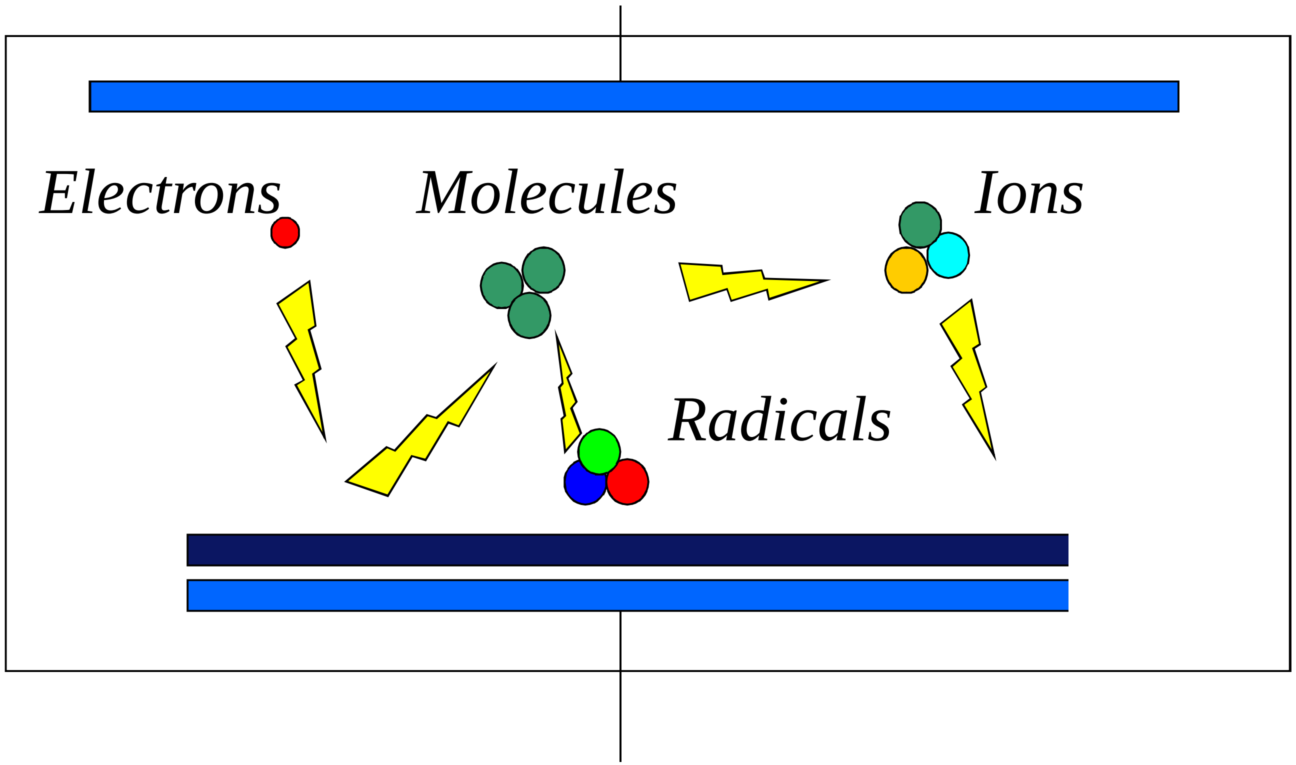
Vartiainen et al. (2003) *Packaging Technology and Science, No: 6, 223 - 229*

Roll-to-roll treatments in coating pilot-line

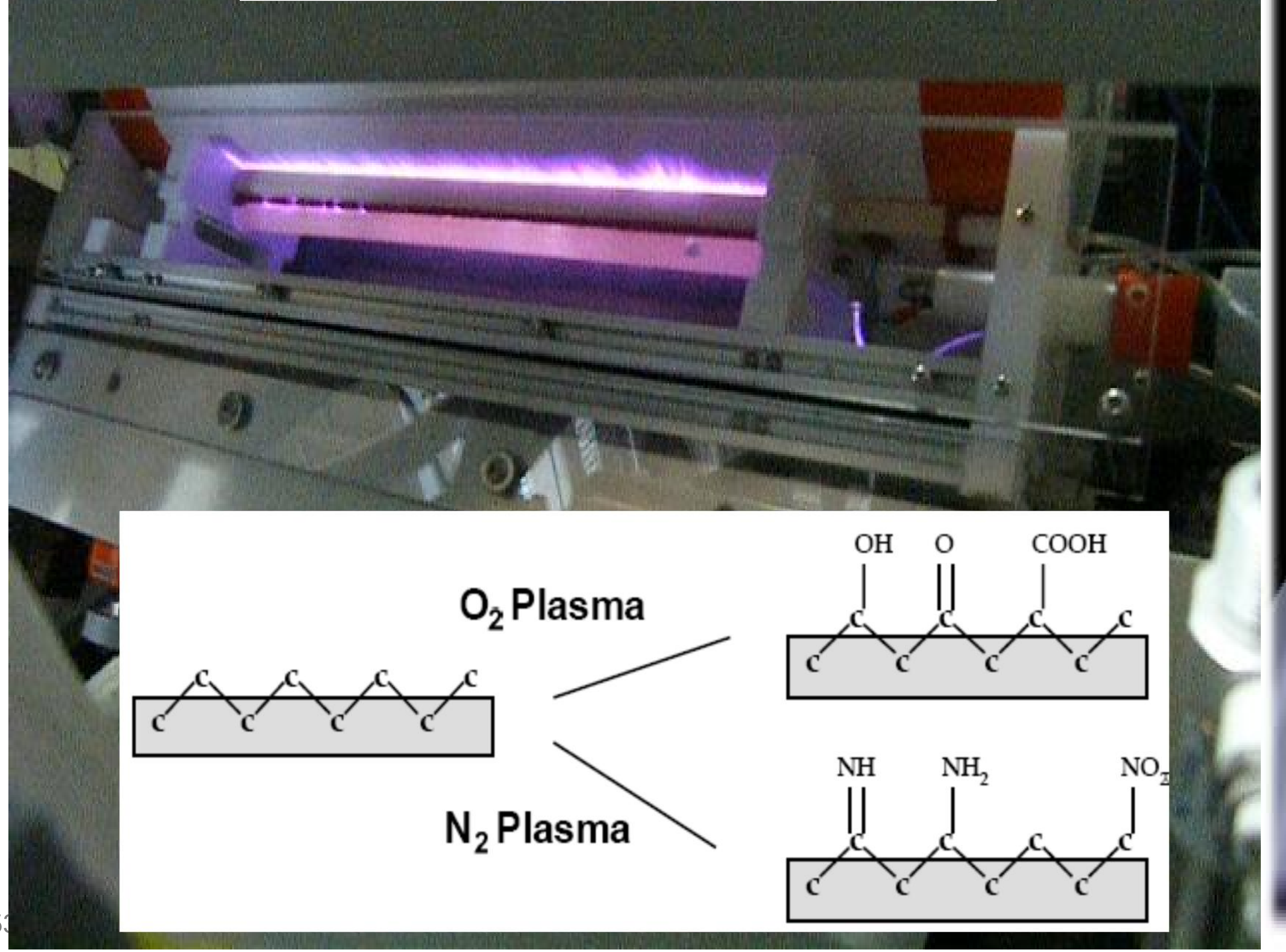


Plasma activation

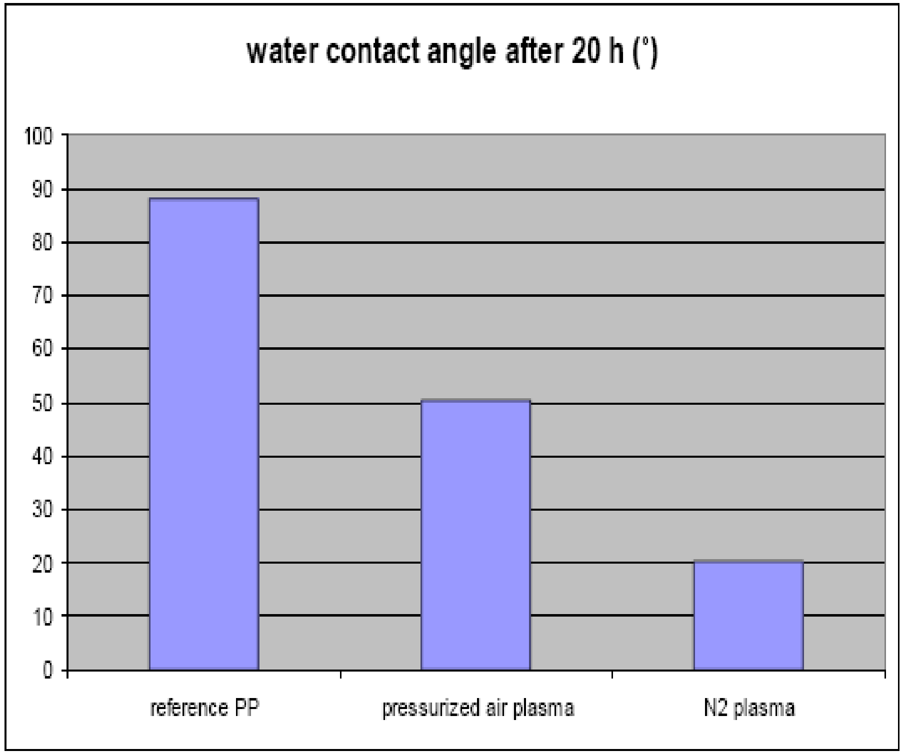
- Plasma is a (partially) ionised gas in which ions and electrons are present as well as radicals and molecules in an excited state
- Plasma contains both physical as well as chemical very reactive species.

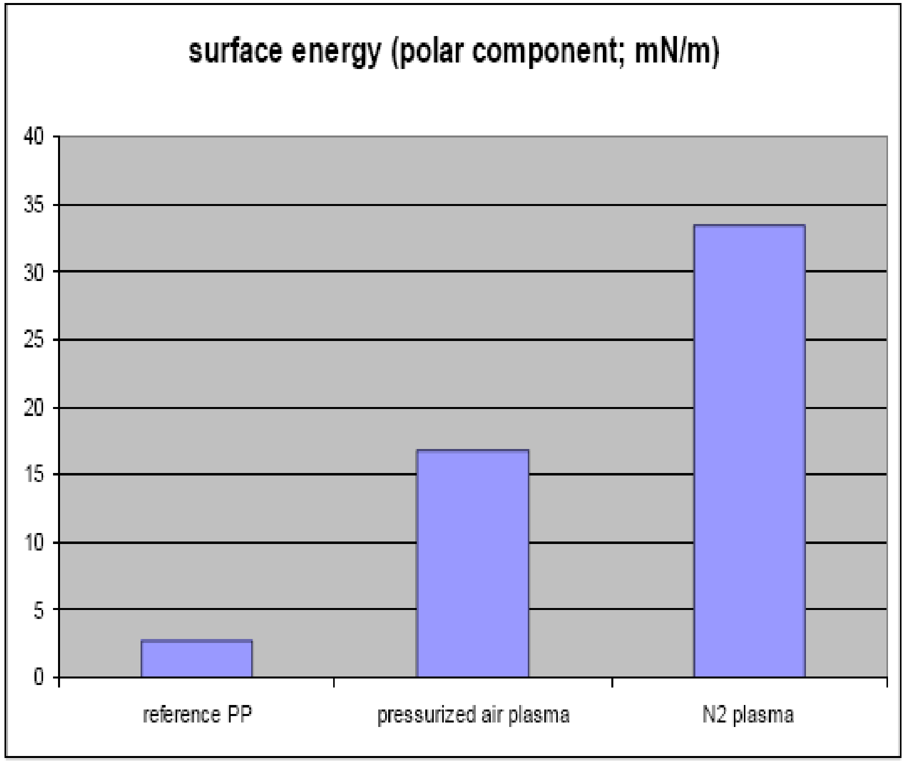


Plasma activation

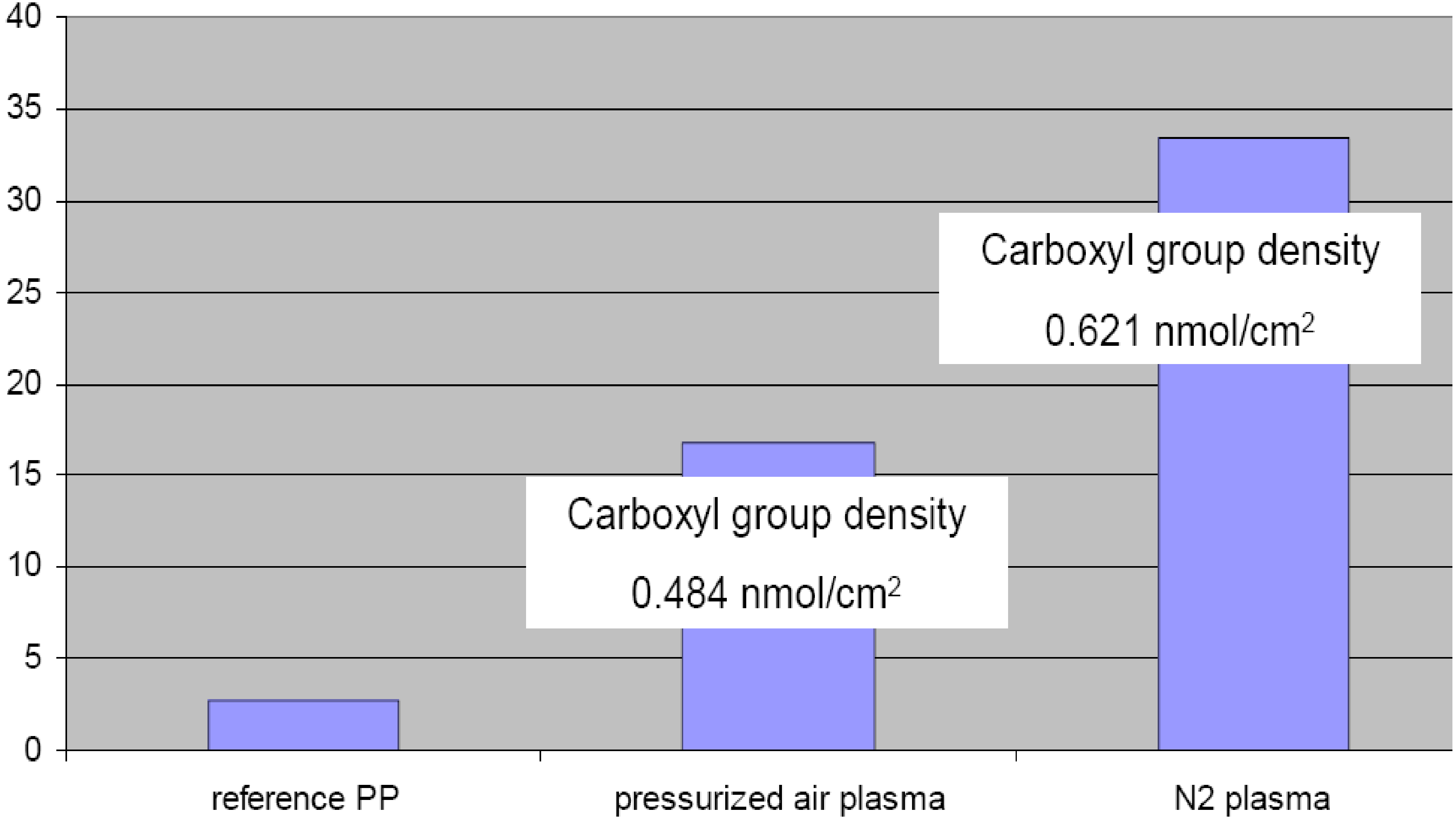


Plasma activation



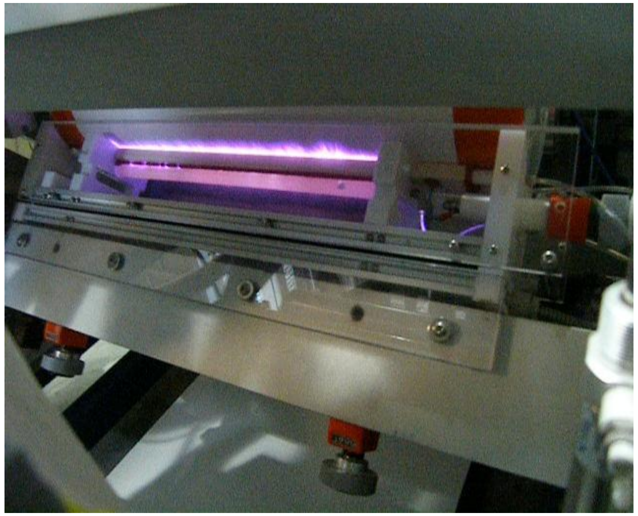


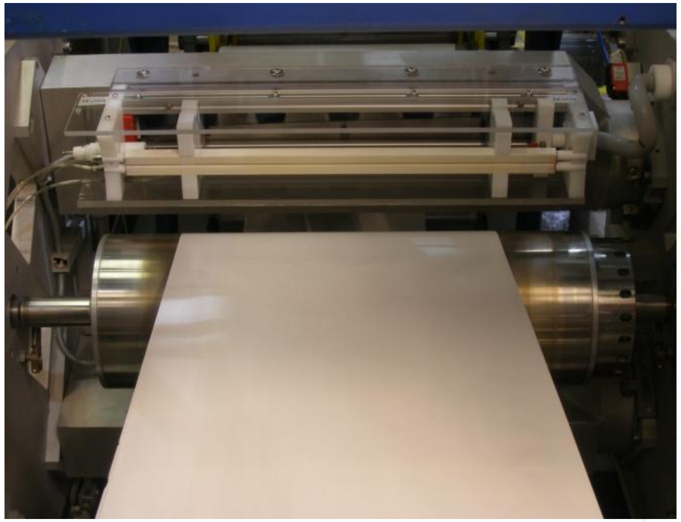
Surface energy (polar component mN/m)



Wet-coating of plasma-activated surfaces with antimicrobial compounds

- Biobased polymers modified with antimicrobial compounds and enzymes





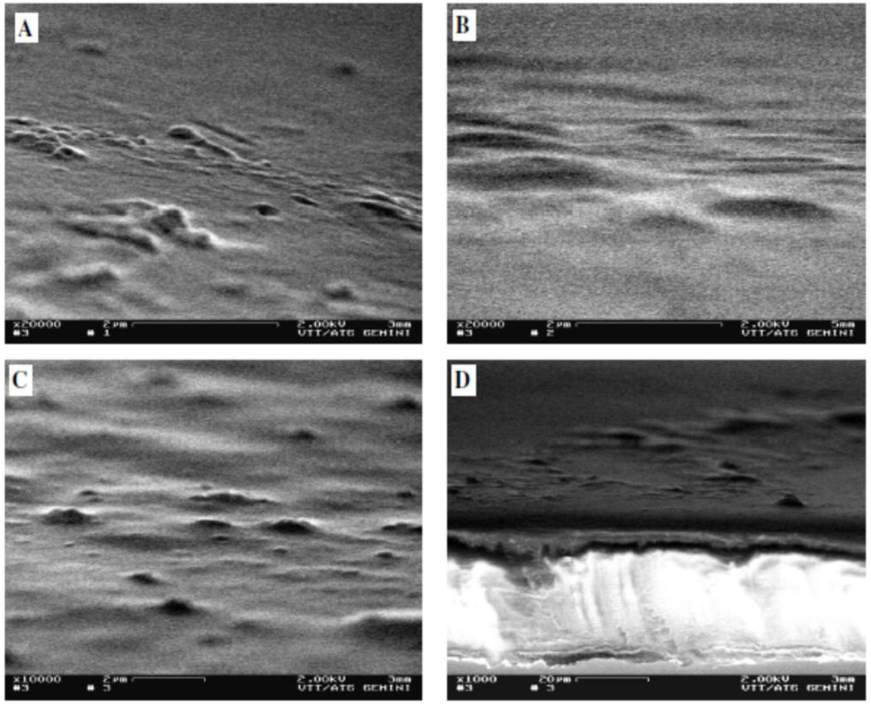


Figure 4. Surface topography of (a) untreated, (b) N_2-plasma + NH_3 treated and (c) chitosan coated, N_2-plasma + NH_3 pretreated BOPP films and (d) cross-section of chitosan coated sample.

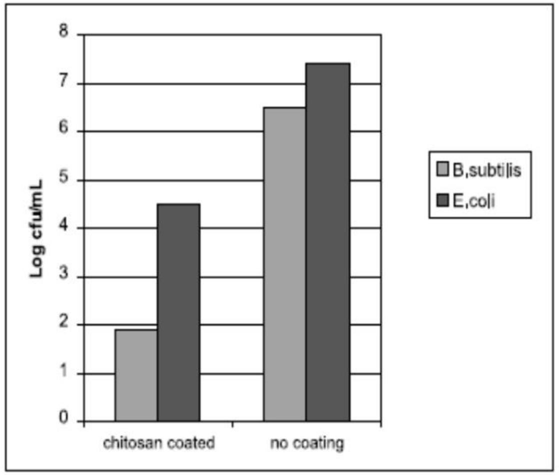


Figure 5. Effect of plasma activated BOPP film with or without surface immobilized chitosan (0.1% glutaraldehyde as linking agent) on survival of *E. coli* and *B. subtilis* (24 h in peptone saline at 30 ºC). Means (n=3).

Table 3. Gas transmissions of BOPP films expressed as $cm^3/(m^2 \cdot 24\ h)$.

Film	Oxygen	Carbon dioxide	Ethylene
BOPP (without plasma)	1500	4000	430
BOPP (N_2-plasma + NH_3)	1500	4600	390
Chitosan coated BOPP (N_2-plasma + NH_3)[a]	27	790	53

Means (n=2)

Vartiainen et.al (2005) *Polymer Bulletin*. Vol. 54 No: 4 - 5, 343 - 352

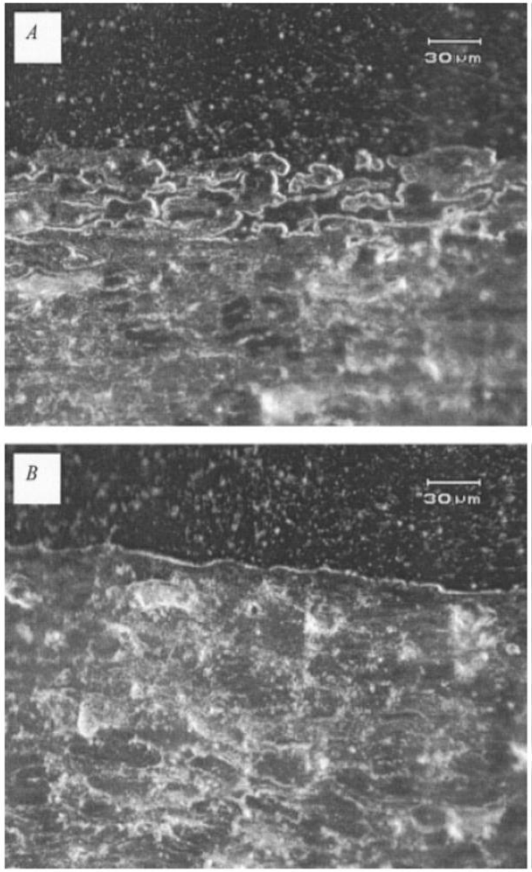
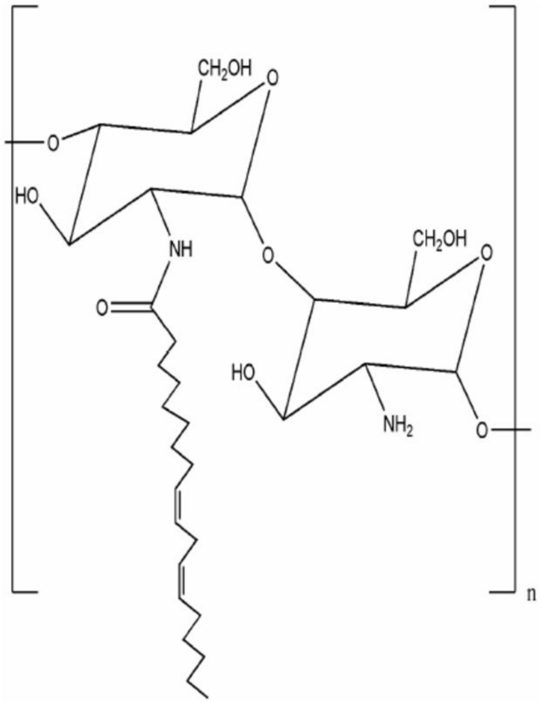


Figure 1 (A) Uncoated and (B) chitosan/6.4% propionic acid coated boards (taken with an Olympus BH-2 microscope equipped with an Olympus DP12 microscope digital camera system).



Vartiainen et al. (2007) 10th Pacific Polymer Conference (PPC 10). Kobe, Japan, 4 - 7 Dec. 2007

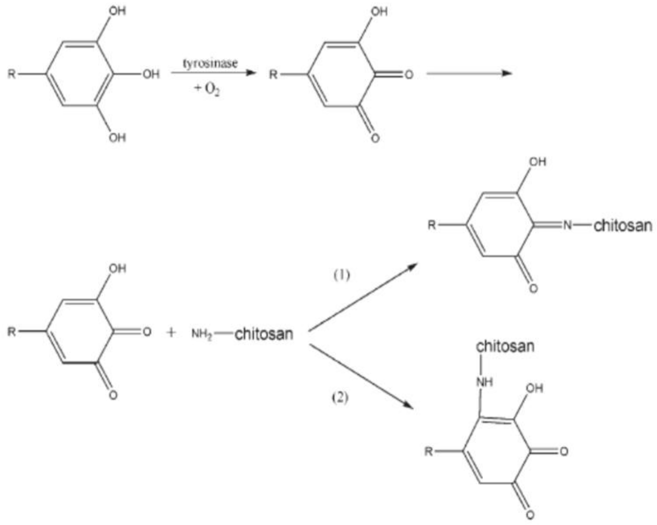


Figure 3. Proposed reactions in tyrosinase-catalysed grafting of gallates to chitosan.

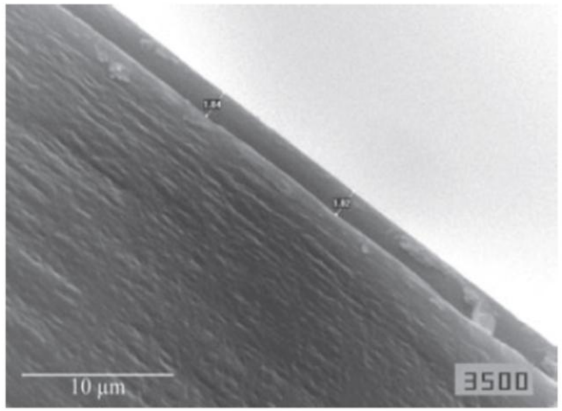


Figure 4. SEM cross-section picture of chitosan-coated plasma-activated BOPP film.

Vartiainen et al. (2004) Journal of Applied Polymer Science. Vol. 94 No: 3, 986 - 993

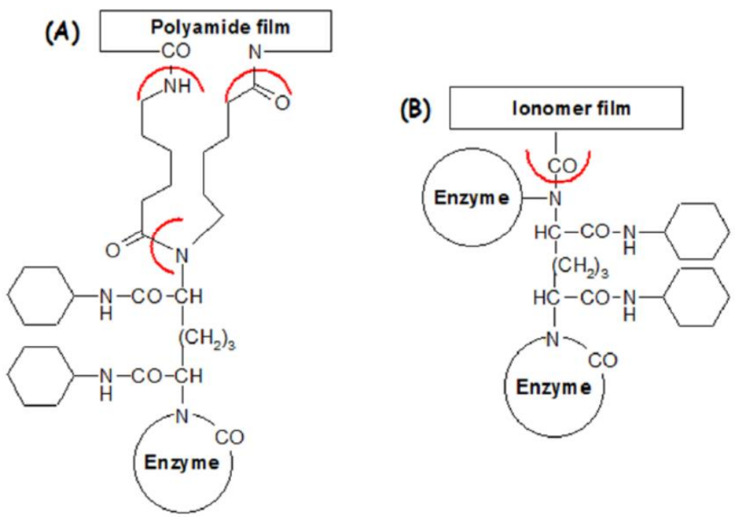
Vartiainen et al. (2008) Packaging Technology and Science. Vol. 21 No: 6, 317 - 328

Central European Journal of **Chemistry**

Development of antimicrobial packaging materials with immobilized glucose oxidase and lysozyme

Research Article

Kristýna Hanušová[1*], Lukáš Vápenka[1], Jaroslav Dobiáš[1], Linda Mišková[2]



The scheme of linkage between enzyme and polyamide film (A) and ionomer film (B) with indication of hypothetical cleavage (dashed curve) of enzyme from polymer.

Storage time (day)	Activity of immobilized GOX (%)	
	Polyamide film	Ionomer film
0	100	100
14	98.3 ± 1.4	97.5 ± 1.1
21	97.1 ± 1.7	95.2 ± 1.9
28	93.6 ± 1.4	80.9 ± 1.8
41	92.1 ± 2.3	77.6 ± 2.0
56	73.8 ± 2.2	60.4 ± 1.3
193	17.5 ± 4.2	15.0 ± 2.5
245	3.1 ± 1.4	5.4 ± 1.6

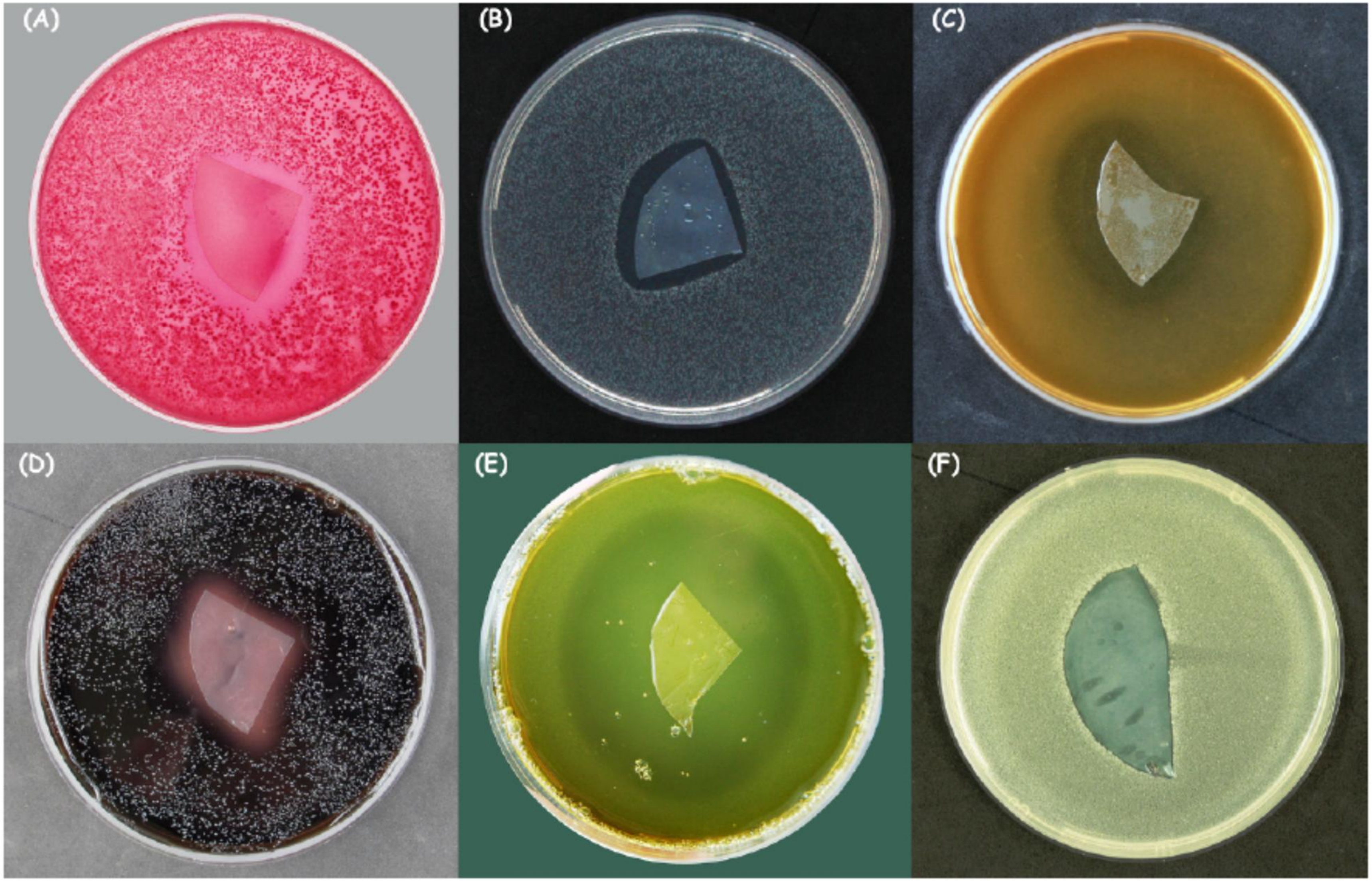
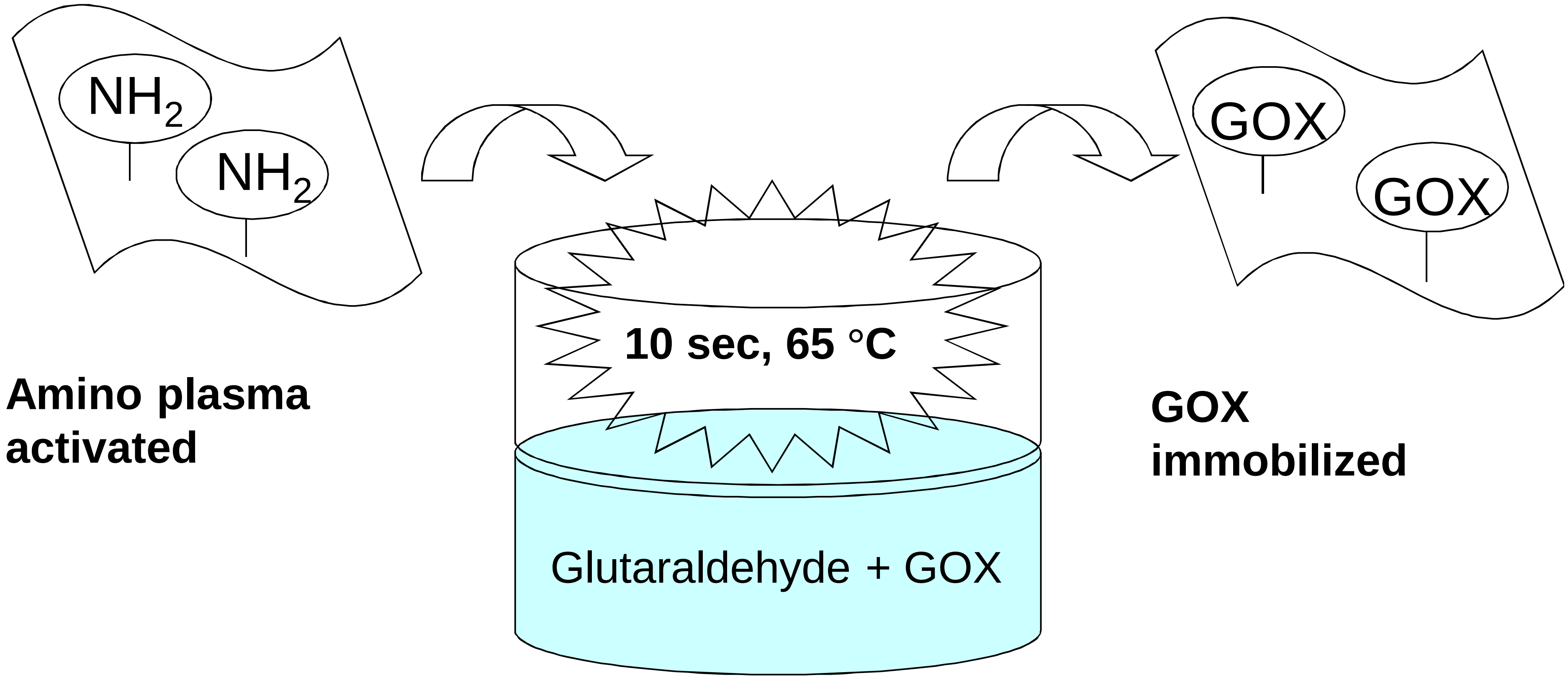
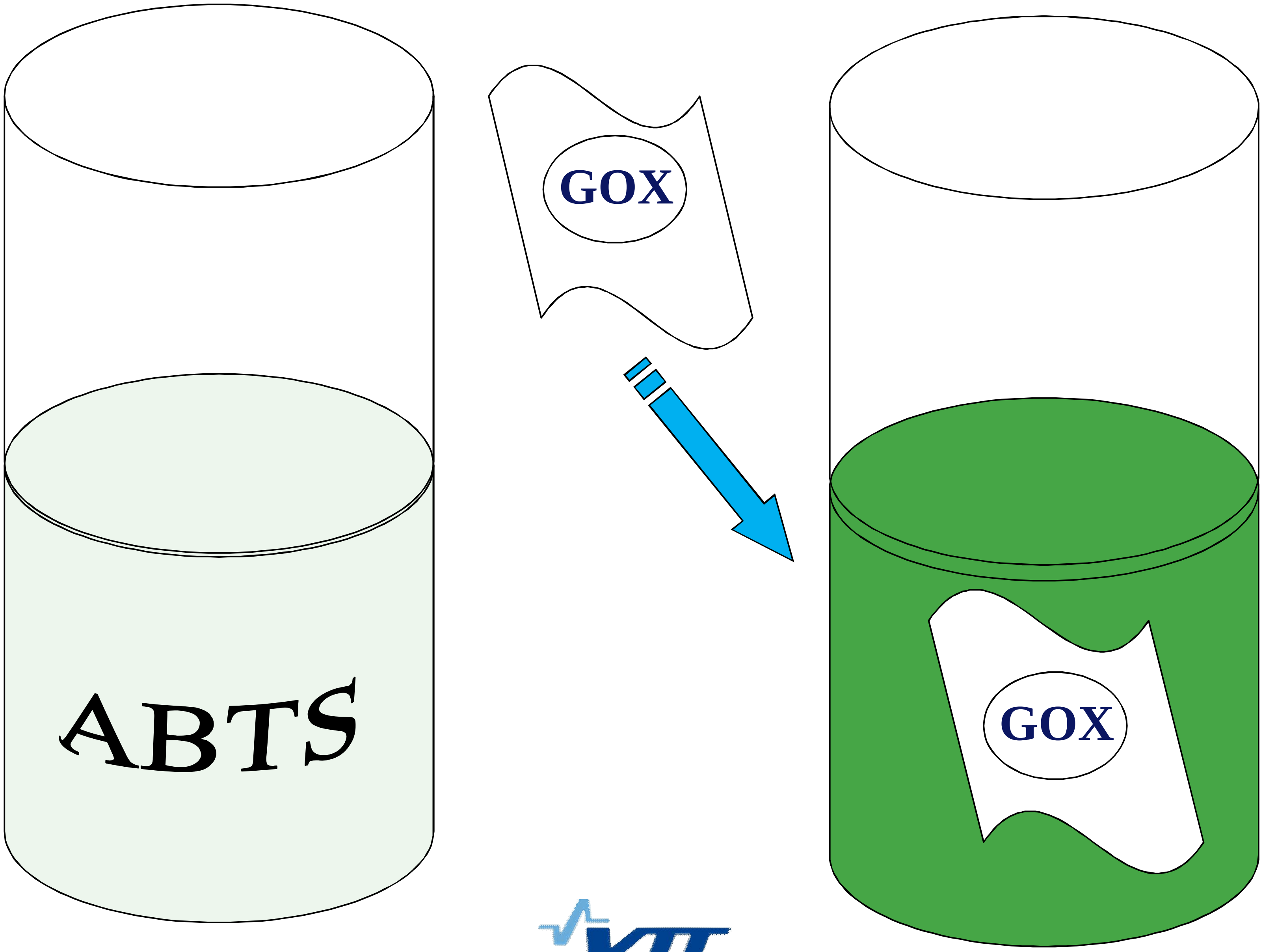


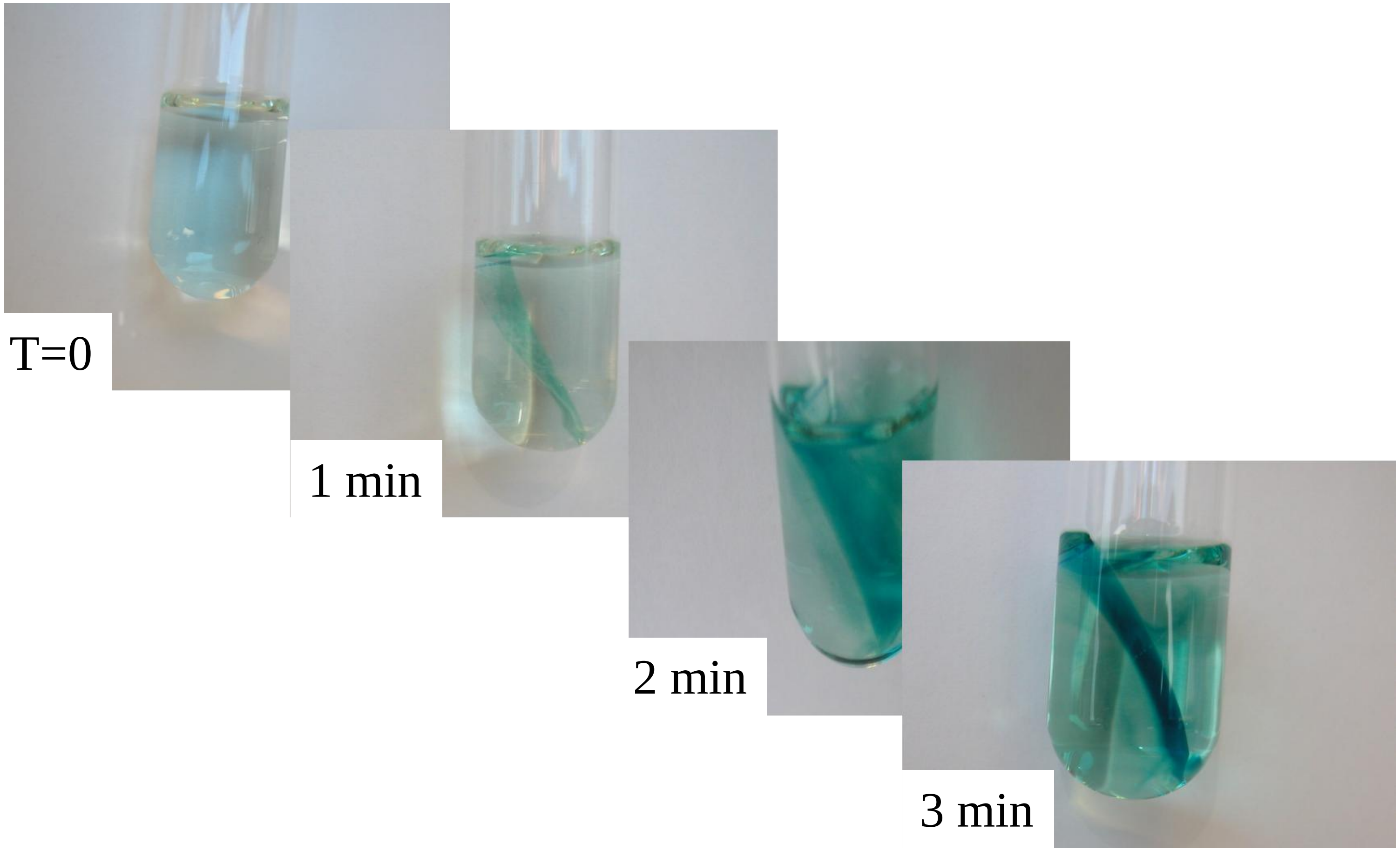
Figure 5. The growth inhibition of indicator bacteria: *Escherichia coli* (A) and *Pseudomonas fluorescens* (B) by ionomer film with GOX; *Lactobacillus helveticus* (C) and *Listeria innocua* (D) by polyamide film with GOX; *Listeria ivanovii* (E) by polyamide film with GOX during cold storage at 4°C; *Bacillus subtilis* (F) by cellulose film releasing LYS.

Immobilization procedure of antimicrobial glucose oxidase




GOX
ABTS
GOX

Glucose oxidase immobilized onto N_2-plasma + NH_3 activated PP



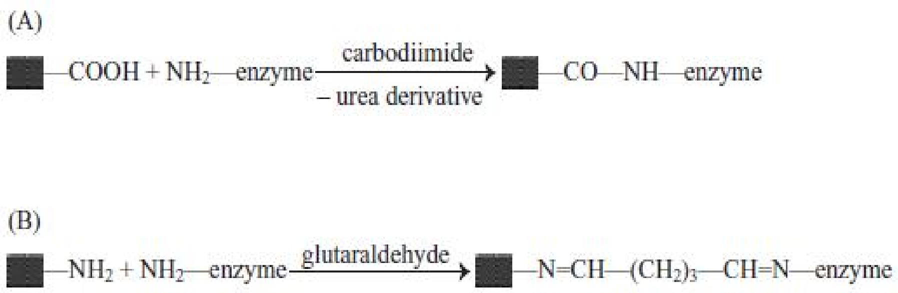
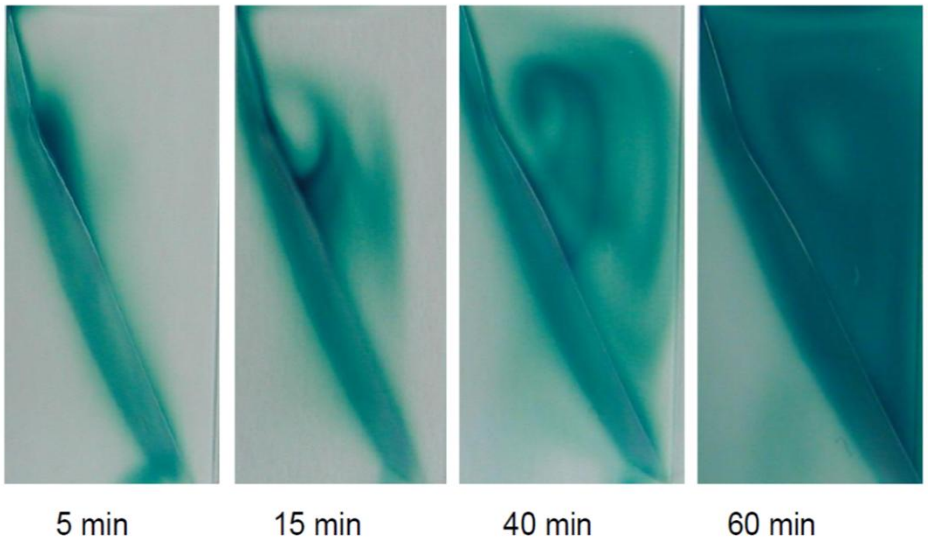


Figure 3. Schematic diagram of immobilization of enzyme (glucose oxidase) onto (A) carboxyl-activated and (B) amino-activated food packaging film (BOPP).



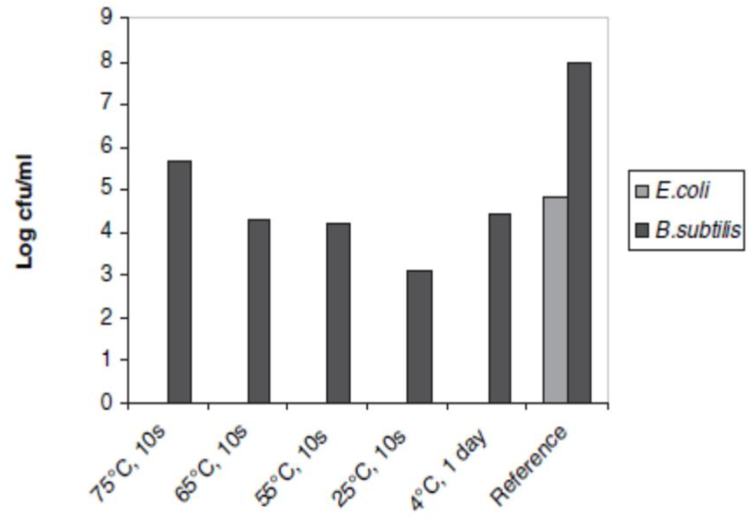
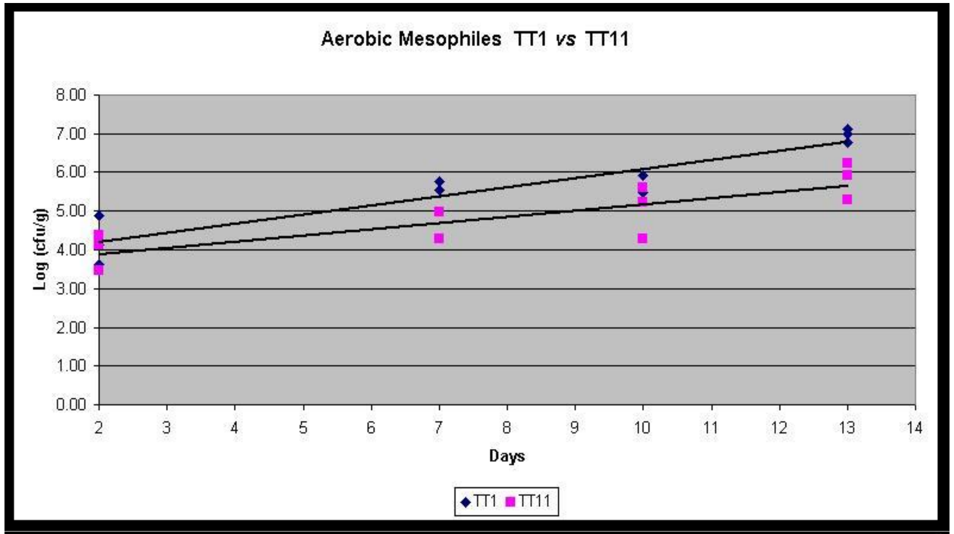
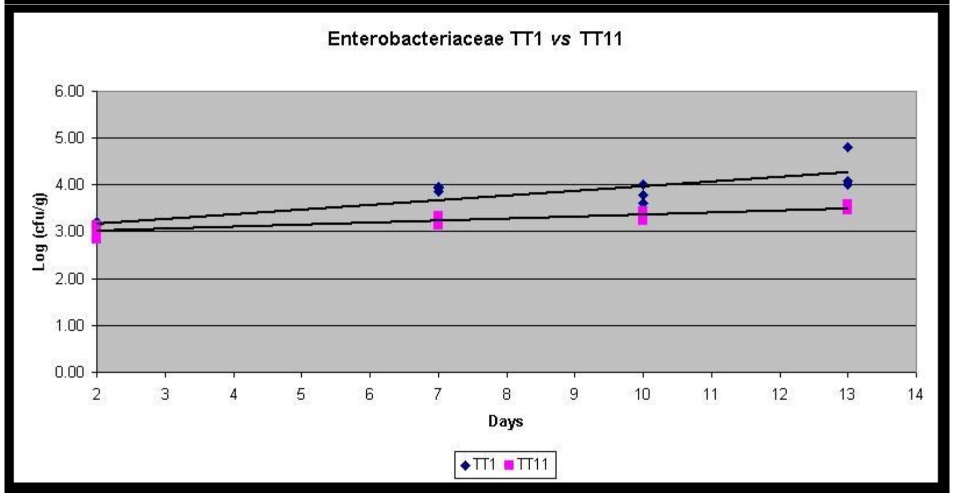


Figure 9. Antimicrobial activity of BOPP films immobilized with glucose oxidase. Immobilization was carried out in phosphate buffer, pH 7.2, containing 2.5% of glutaraldehyde for 10 s at 25°C, 55°C, 65°C and 75°C, or for 1 day at 4°C. Films were incubated for 24 h at 30°C. Means (n = 2).

Vartiainen et al. (2005) Packaging Technology and Science. Vol. 18 (2005) No: 5, 243 - 251

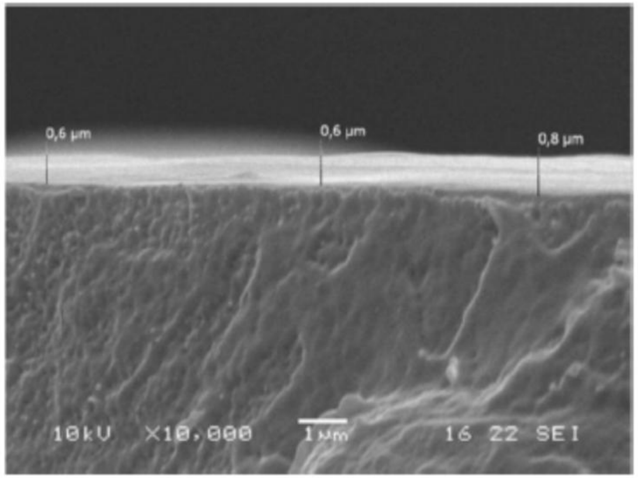
Chicken breast fillets packed into plasma-activated film immobilized with two natural antimicrobial peptides





Gelatin coating with two natural antimicrobial peptides

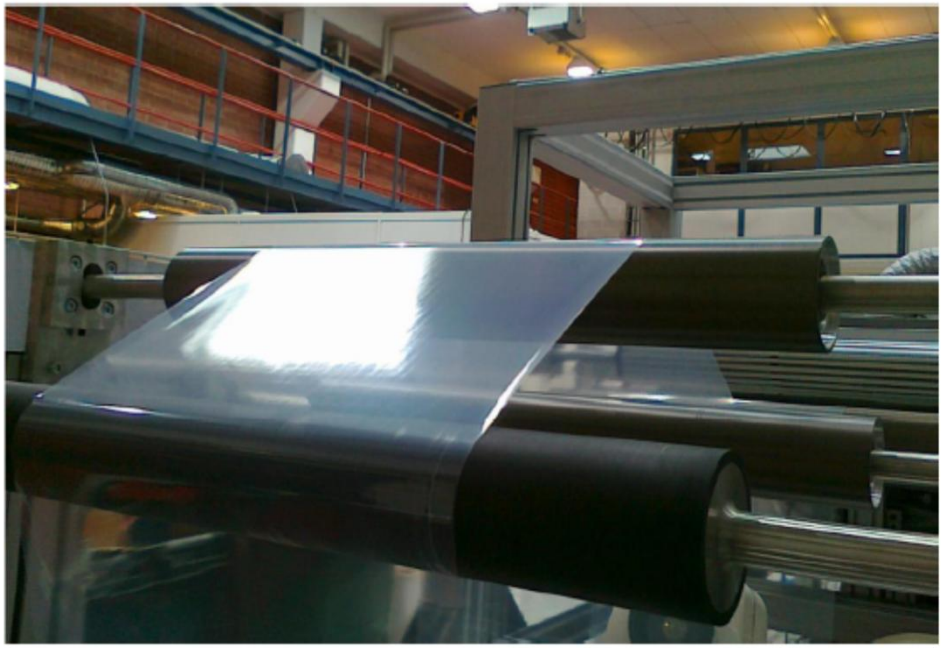
- Speed 5 m/min
- Corona treatment prior to gelatin coating
- Coating was applied onto PE surface
- Flexo-coating unit was tempered (50°C)



Gelatin coating with two natural antimicrobial peptides

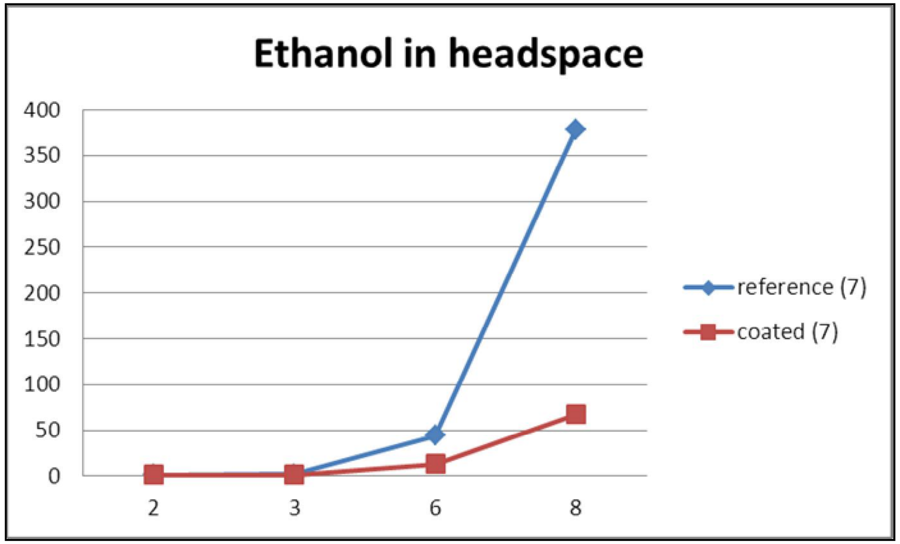
- Drying with 5 air dryers at 80°C
- Totally 738 m (top film; width 355 mm) and 461 m (down film; width 360 mm) were coated with gelatin
- Approx. 1 g/m^2

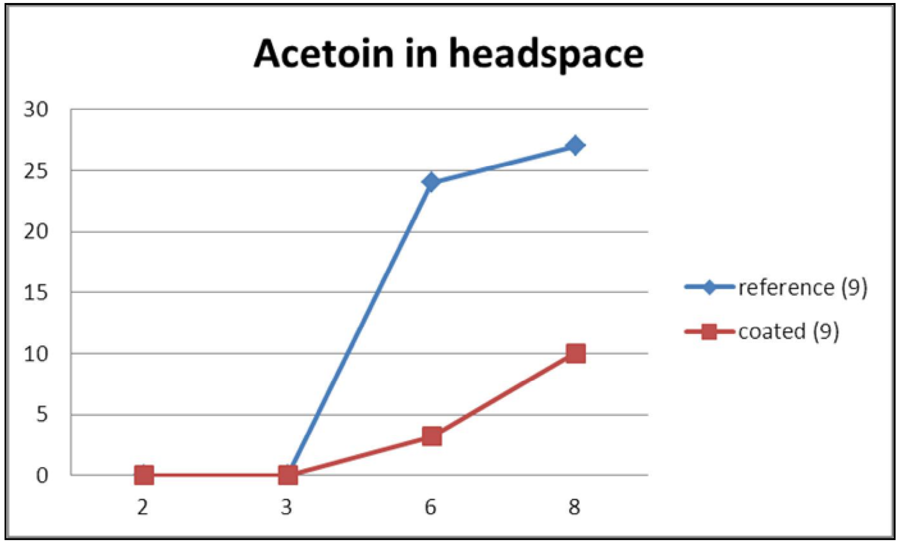
→ **Antimicrobial vacuum packaging for fish**

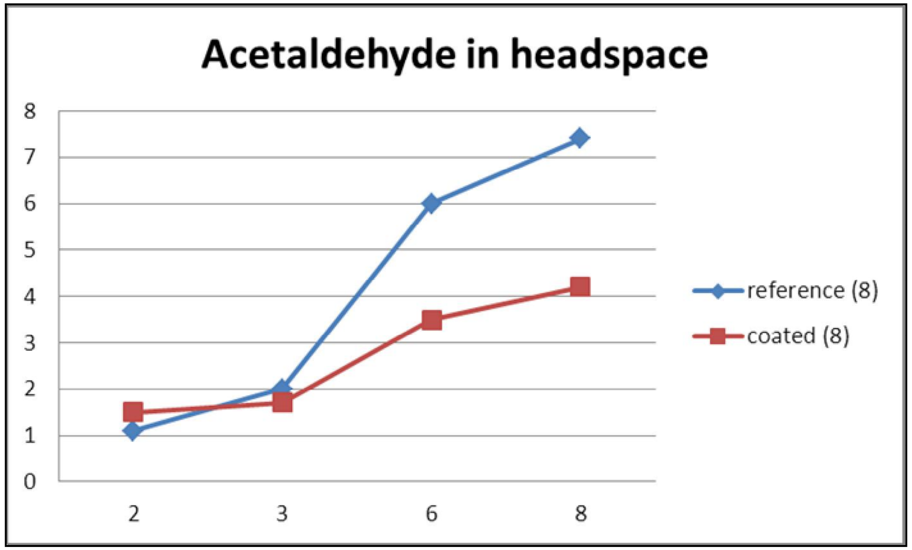


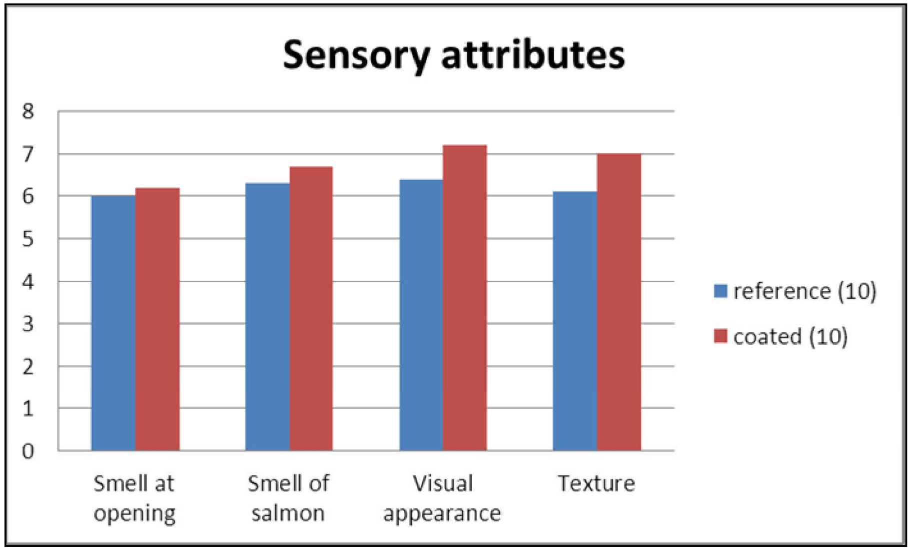
Vacuum-packed fresh salmon fillet

- Pouches of the dimension 25 x 15 cm were prepared.
- Fresh salmon fillets, with a weight of approximately 200 g each, were packaged individually and sealed under vacuum.
- Microbiological, chemical and sensory analyses were carried out after storing at 2˚C for 8 days.

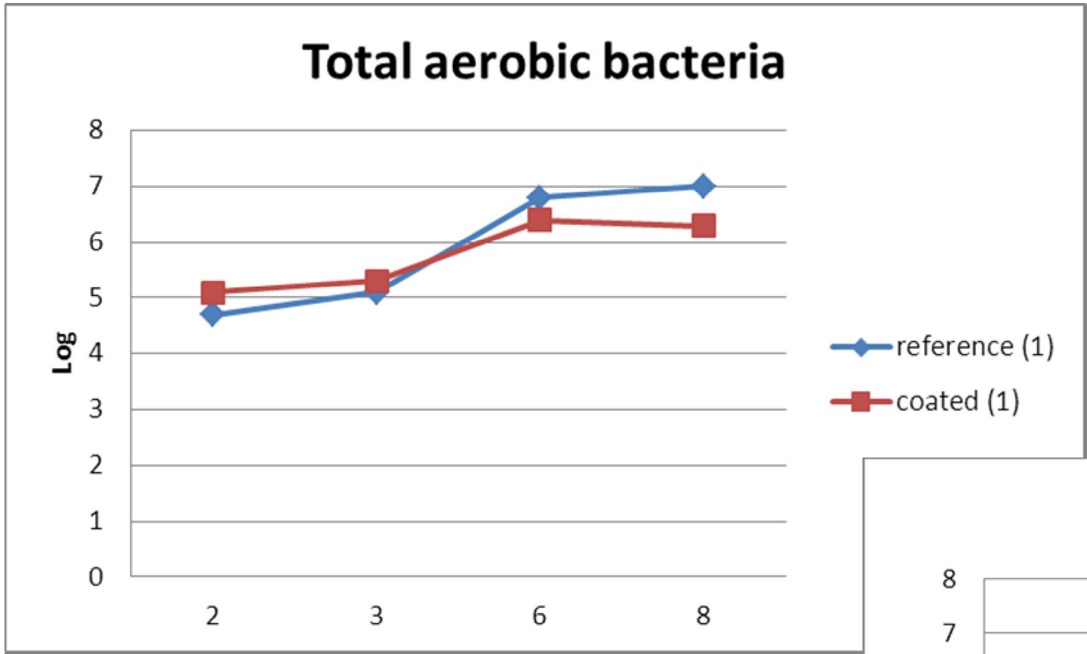

Ethanol in headspace
400
350
300
250
200
150
100
50
0
2
3
6
8
reference (7)
coated (7)

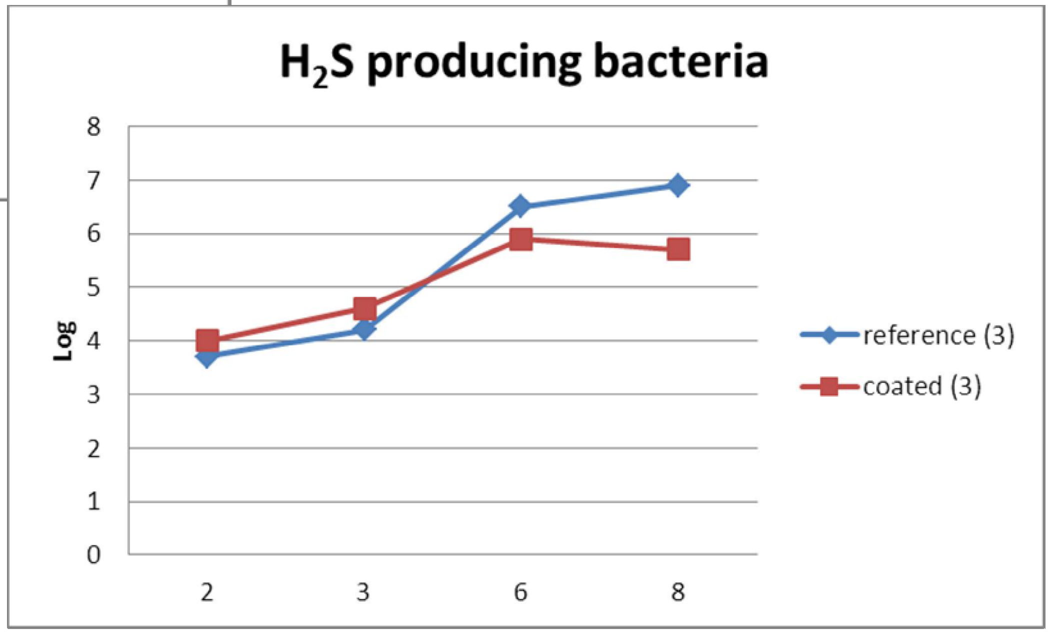

Acetoin in headspace
30
25
20
15
10
5
0
2
3
6
8
reference (9)
coated (9)


Acetaldehyde in headspace
8
7
6
5
4
3
2
1
0
2
3
6
8
reference (8)
coated (8)


Sensory attributes
8
7
6
5
4
3
2
1
0
Smell at opening
Smell of salmon
Visual appearance
Texture
reference (10)
coated (10)

Antimicrobial activity

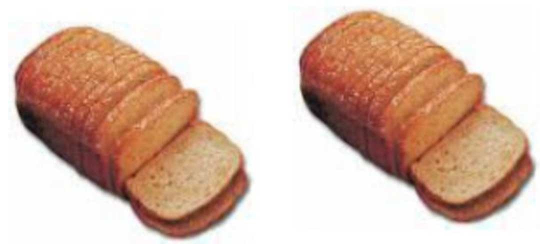




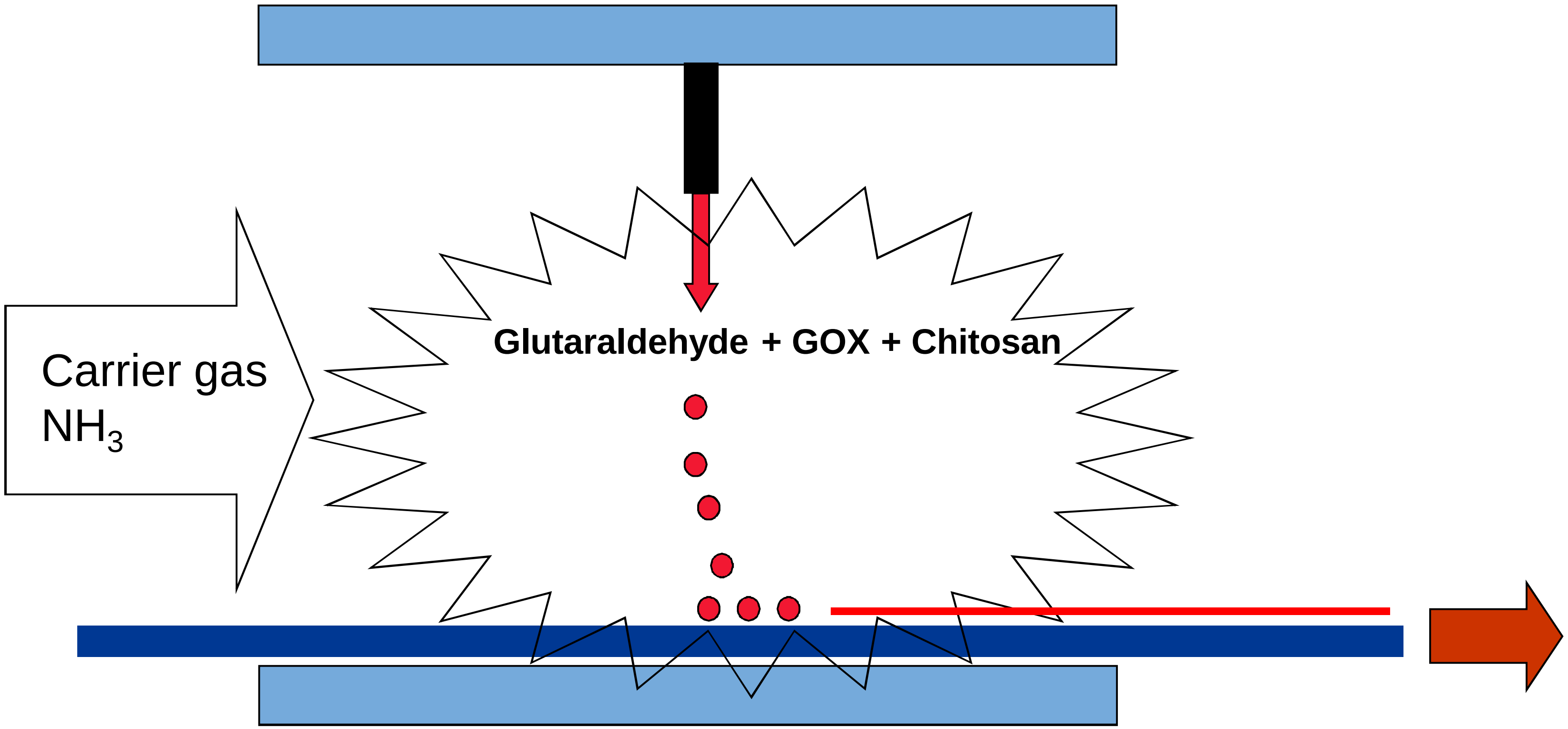
Some examples of VTT research results

- Antimicrobial treatments for sausage casings
    - Activity against *Listeria*

- Antimicrobial printing inks for bread packaging
    - Activity against bread spoiling moulds



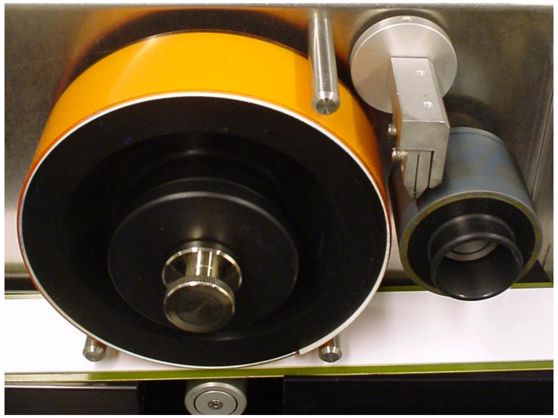
Immobilization procedure using atmospheric plasma



Amino activation **GOX/Chitosan immobilization**

Antimicrobial printing

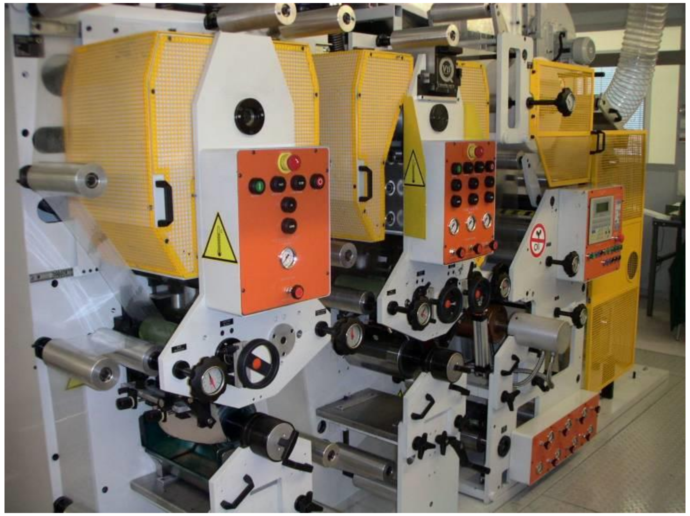
Target: To develop ink with antimicrobial properties applicable with conventional printing technique (flexo or rotogravure) to food packaging material.



Inner surface of the packaging material is covered with an antimicrobial ink layer coming in contact with packed foodstuffs.

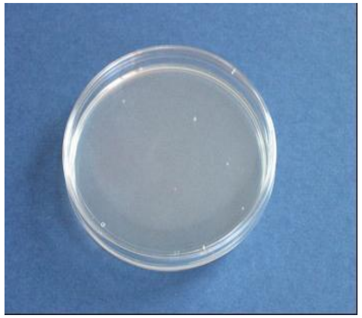
Antimicrobial printing: advantages

- Thin active layers
  - total amounts of antimicrobial substances as low as possible
- Traditional printing method
  - flexo or rotogravure
- No high temperatures
  - higher antimicrobial activity
- Easy to apply
  - whenever, wherever…



Functionalization of paper by adding inorganic TiO_2 and ZnO nanoparticles

- TiO_2 and ZnO have photo-oxidative and antimicrobial activities
  - Inhibition to grow (bacteriostatic) or killing (bactericidal) of patogenic bacteria: gram- , gram+ and bacteria spores.
- TiO_2 40 nm nanoparticles and ZnO 45 nm nanoparticles



Nano-composite	Initial mixing ratio of the preparations (as dry weight)	TiO_2 content (% dry weight)	ZnO content (% dry weight)
CNF-TiO_2	**1 : 1**	**24**	**-**
CNF-ZnO	**10 : 1**	**-**	**7**
CNF-ZnO&TiO_2	**10 : 1 : 10**	**42**	**2**

Nano-composites preparation:

- 15 min mixing CNF suspension (2.5% in water) with TiO_2 (6% in water) and/or ZnO (1% in ethylene glycol)
- 3 washings with water followed by centrifugation to eliminate not-adsorbed inorganic fillers

Antimicrobial paper

Antibacterial activity under conditions of light exposition.
Bacteria grow on untreated reference: $10^6 – 10^7$ (6-7 log).

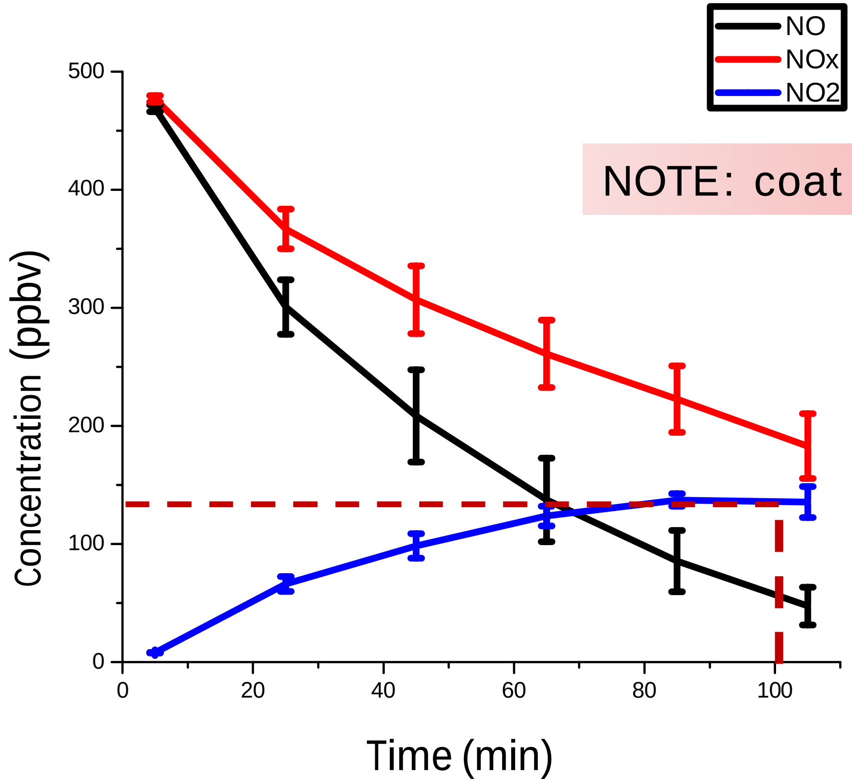
Paper Samples	ppm ZnO	% TiO_2	*S. aureus (Gram +)*		*K. pneumoniae (Gram -)*	
			Bacteriostatic activity (log reduction)	Bactericidal activity (log reduction)	Bacteriostatic activity (log reduction)	Bactericidal activity (log reduction)
Untreated paper (control)	0	0	0	0	0	0
Paper CNF-TiO_2 (0.4 g/m^2)	0	0.034	0	0	0	0
Paper CNF-TiO_2 (0.9 g/m^2)	0	0.167	1.3	0	0	0
Paper CNF-TiO_2 (1.8 g/m^2)	0	0.291	Total bacteriostatic	1.0	1.8	0
Paper CNF-ZnO&TiO_2 (0.6 g/m^2)	38.4	0.115	0.7	0	0	0
Paper CNF-ZnO&TiO_2 (1.3 g/m^2)	104.6	0.307	Total bacteriostatic	0.1	0.2	0
Paper CNF-ZnO (0.8 g/m^2)	180	0	Total bacteriostatic	0.3	2.1	0

- Significant **bacteriostatic activity** was obtained (inhibition to bacteria proliferation) with TiO_2 contents around 0.3%
- Bactericidal activity (bacteria killing-reduction of initial inoculated cells) was not detected.

- **Patrizia Sadocco(*), Jessica Causio(*), Giovanni Baldi(**)(*) Innovhub-SSCCP, (**) Centro Ricerche Colorobbia Italia**

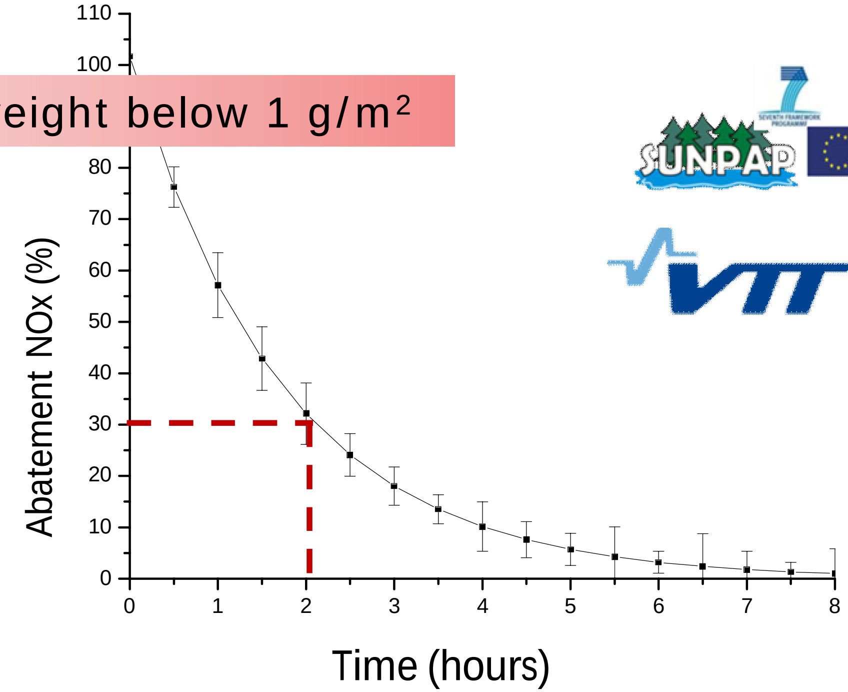
Active paper for the photo-oxidation of volatile substances in gaseous phase

Kinetic of NOx photodegradation in gaseous phase by CNF-TiO_2 foam coated paper



NOTE: coat weight below 1 g/m^2

Abatement NOx



Around 70% NOx oxidation within 100 minutes

ØCNF-TiO_2 has significant activity for the oxidation of NO and NOx

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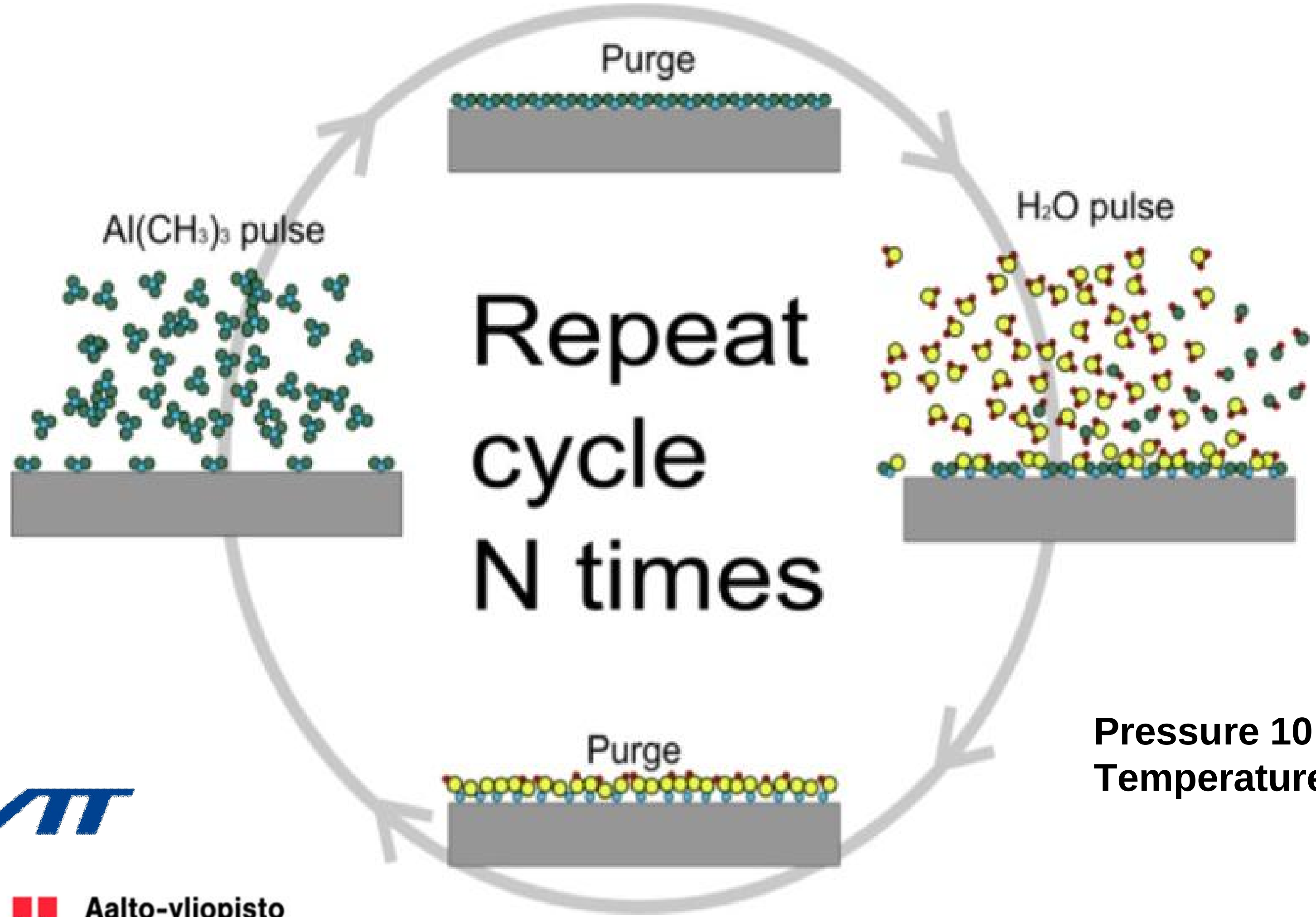
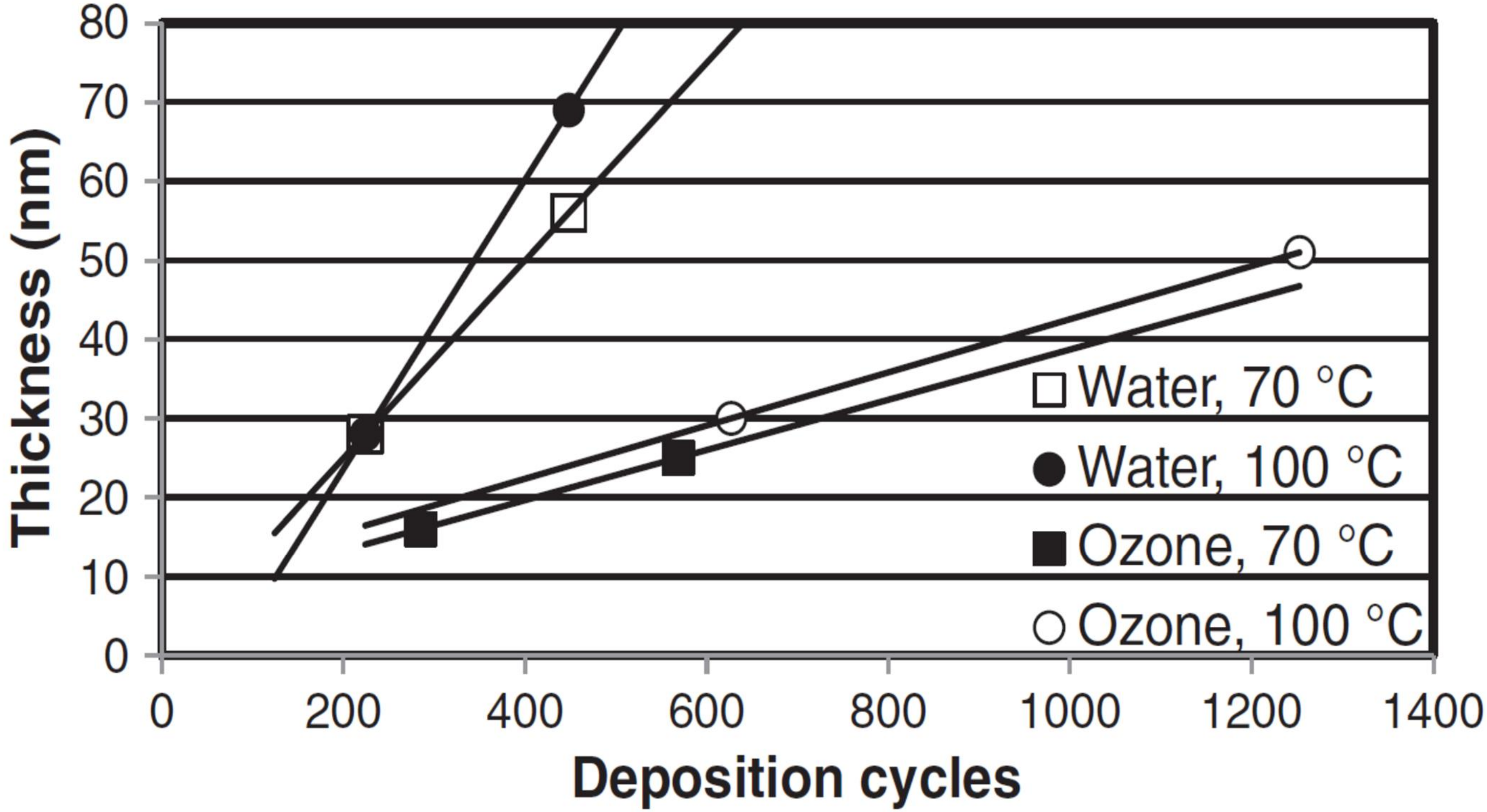
ALD; Repeated Self-Limiting Gas-Solid Reactions



Pressure 10 Pa - 100 kPa;
Temperature 50-500 °C

Aalto-yliopisto

Picture by Aalto University



Thickness (nm)
80
70
60
50
40
30
20
10
0
0
200
400
600
800
1000
1200
1400
Deposition cycles
Water, 70 °C
Water, 100 °C
Ozone, 70 °C
Ozone, 100 °C

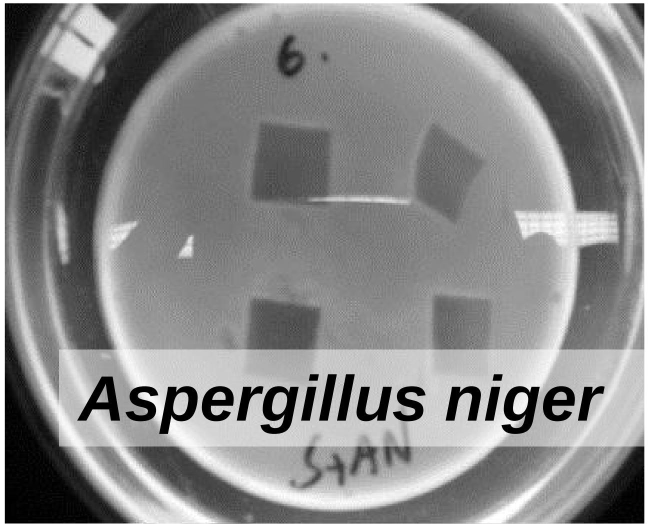
Antimicrobial activity

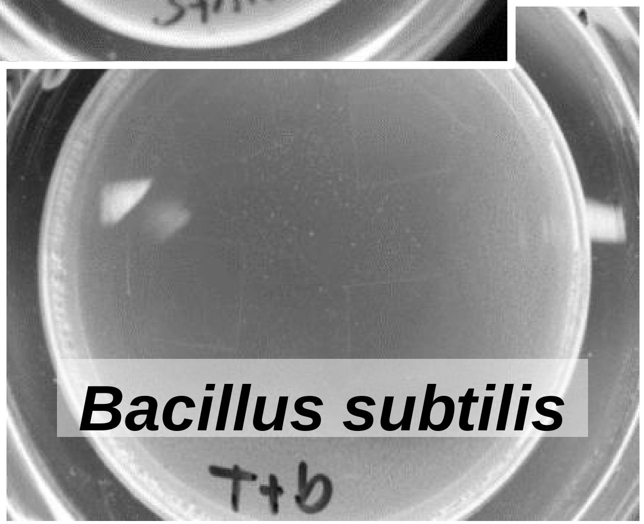
Thin coatings	Activity
25 nm Al_2O_3 (water) 70 °C	3.5
25 nm ZnO (water) 70 °C	5.9
50 nm ZnO (water) 70 °C	5.8
75 nm ZnO (water) 70 °C	5.8
50 nm ZnO + 5nm Al_2O_3 70 °C	5.9
50 nm ZnO + 15nm Al_2O_3 70 °C	4.6
25 nm ZnO (water) 100 °C	2.3
50 nm ZnO (ozone) 70 °C	5.8
50 nm ZnO (ozone) 100 °C	5.8

- Determined with JIS Z 2801,
- Antimicrobial if activity > 2,
- All samples antimicrobial against *Escherichia coli,*
- Direct contact rather than edge diffusion more efficient,
- Nanolaminate consisting of 50 nm ZnO covered with a layer of Al_2O_3 retained most of its antimicrobial activity compared to plain ZnO.

M. Vähä-Nissi et al. / Thin Solid Films 562 (2014) 331–337

Antimicrobial activity





- 50 nm of ZnO deposited onto BOPLA with water at 70 °C indicated lateral diffusion of an antibacterial agent from a relative thick film
- Growth of *Aspergillus niger* and *Bacillus subtilis* inhibited
- EN 1104 (Hemmhof test) test commonly applied to evaluate materials for food contact


TECHNOLOGY FOR BUSINESS