

Packaging Plastics and Nanotechnology

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Sabancı University

Founder Member

Nanotego Co.

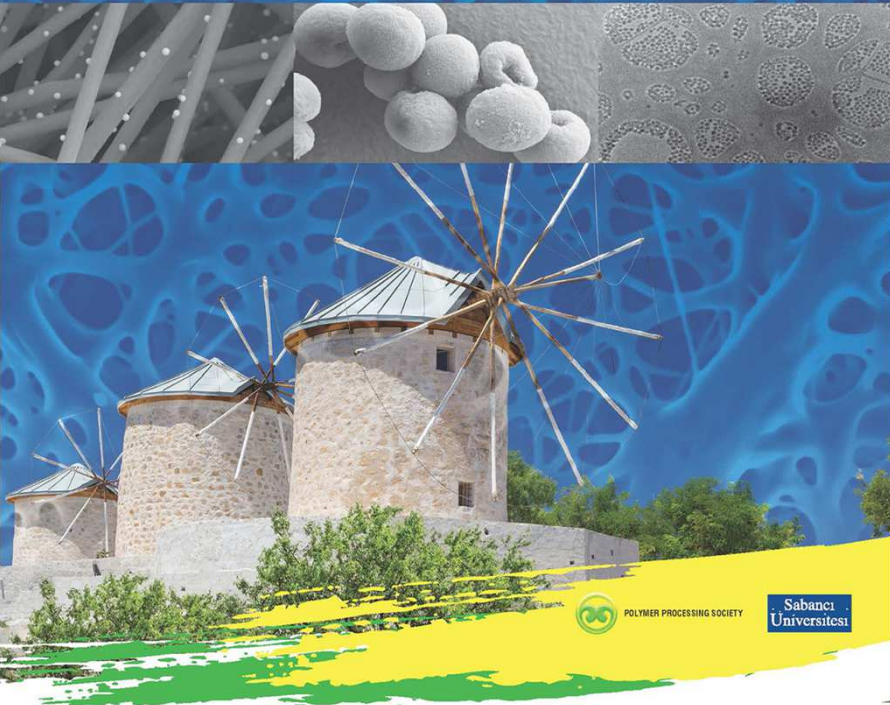


PPS-35

35th INTERNATIONAL CONFERENCE of THE
POLYMER PROCESSING SOCIETY

26 - 30 MAY 2019 • Çeşme-İzmir / TURKEY

Cesme awaits you for the PPS-35



ORGANIZING SECRETARIAT

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PAGEV Sponsored Polymer Processing School

Two days Polymer Processing Course will be held on May 25-26, 2019, the topics are

Raw Materials and Rheology on May 25th

Rheology- C Macosco -Univ Minnesota and G Fuller- Stanford Univ

Compounding- I Manas -Case Western Univ

Process Technologies on May 26th

Injection Molding - M Çakmak Purdue Univ, Y Ülçer, Ravago and M Bilgili-Consultant

Rubber Processing - A I Isaev - Univ of Akron

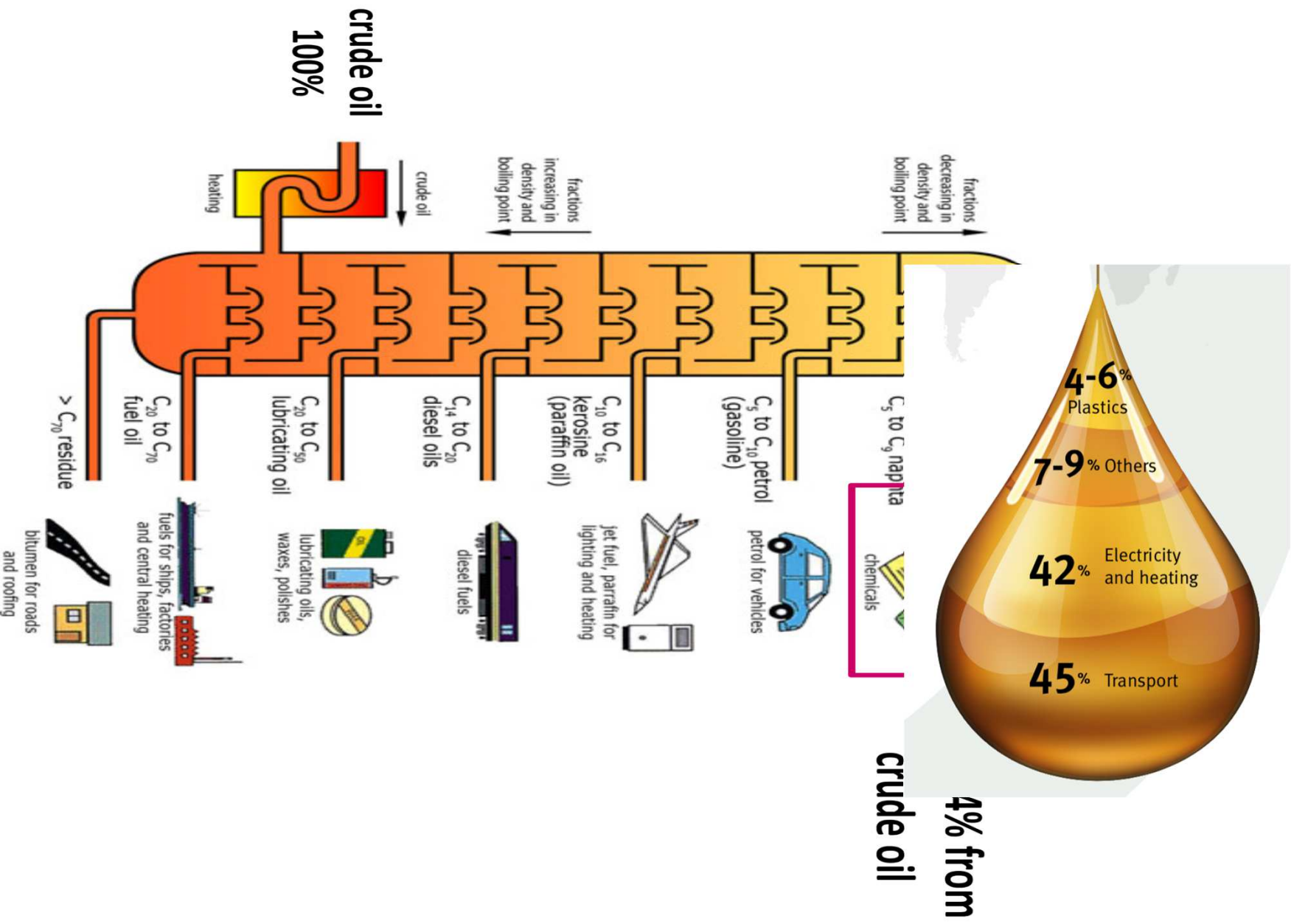
Extrusion- D Kalyon- Stevens Inst of Technology

Composite Processing - C Altan-Univ Oklahoma

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THE NEW PLASTICS ECONOMY: RETHINKING THE FUTURE OF PLASTICS

- The New Plastics Economy — Rethinking the future of plastics (2016, <http://www.ellenmacarthurfoundation.org/publications>).
- Plastics – the Facts 2017
 - An analysis of European plastics production, demand and waste data
- American Chemistry Council
(<https://plastics.americanchemistry.com/default.aspx>)



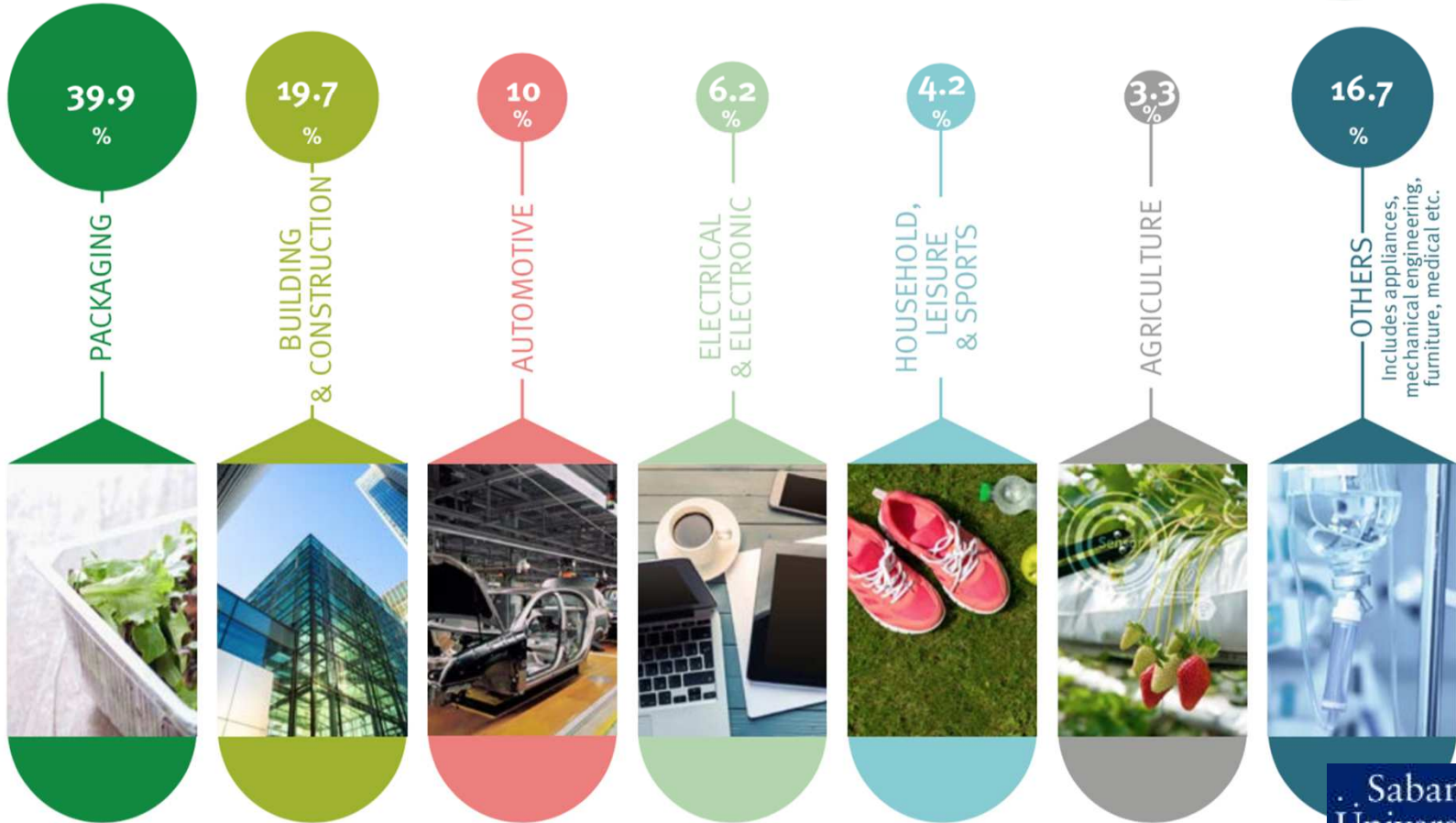
PACKAGING

- Its Primary Role is to contain, protect and preserve
- Delivery System for Products
- Environmental impact is much, much less than that of the damage that would arise without it

Plastics converter demand main market sectors

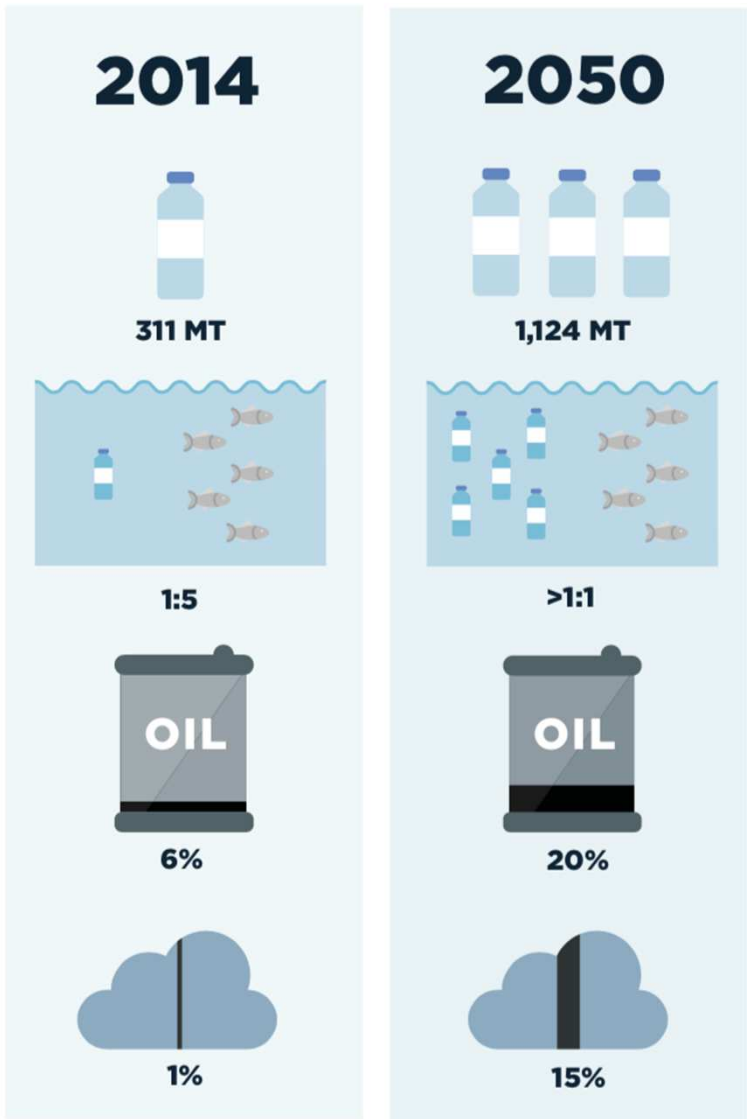
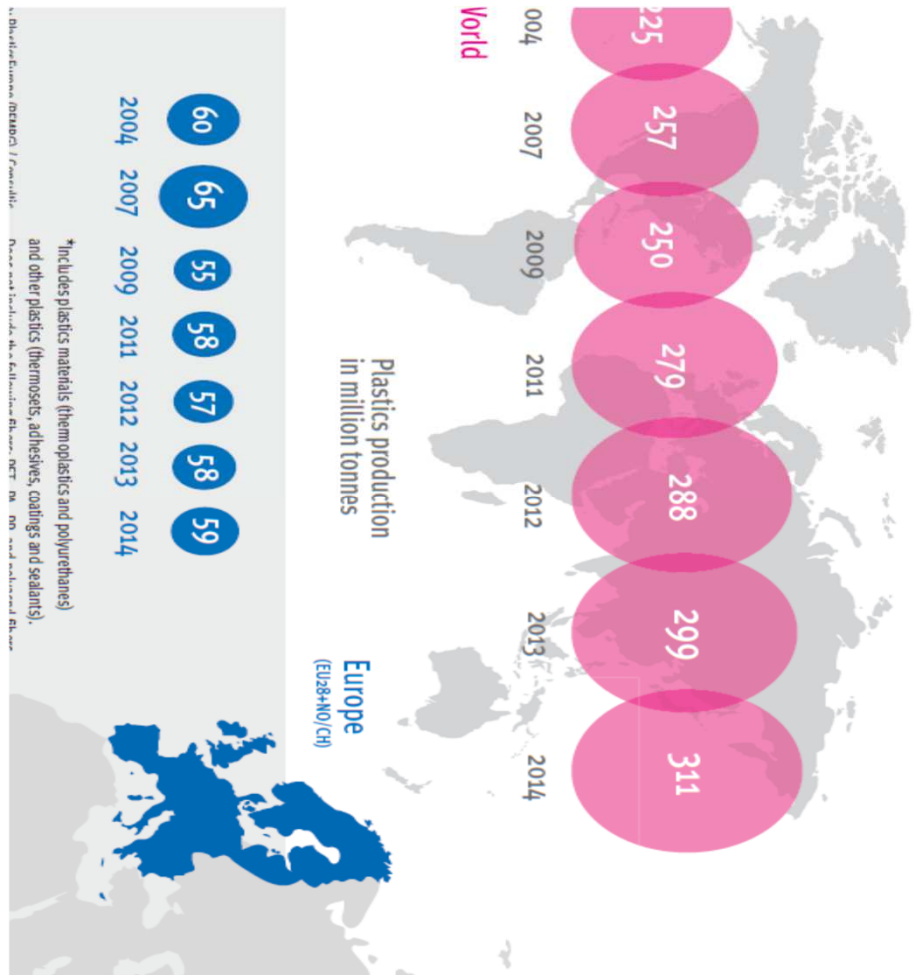
Distribution of European (EU28+NO/CH) plastics converter demand by segment in 2016.
Source: PlasticsEurope Market Research Group (PEMRG) and Conversio Market & Strategy GmbH

Total
converter demand
49.9 m t



Plastics* production is stable in Europe and grows globally

Europe Plastic Demand



PLASTICS PRODUCTION

RATIO OF PLASTICS TO FISH IN THE OCEAN¹ (BY WEIGHT)

PLASTICS' SHARE OF GLOBAL OIL CONSUMPTION²

PLASTICS' SHARE OF CARBON BUDGET³

Examples of How Plastics Are Helping Reduce the Environmental Footprint of Consumer Goods



Reducing Food Waste Through Plastic Packaging

Food waste presents significant financial and environmental impacts. But plastic food packaging has the ability to help prevent food waste, save money, and reduce environmental effects. Plus it helps keep foods fresh and sanitary.¹

Preventing Food Waste

Foods without packaging are thrown out uneaten more often than foods protected by packaging.

Think about the items in a typical refrigerator. Fruit and veggies tightly sealed in protective plastic are more likely to reach the dinner table than unpackaged fruit and veggies.



¹ Study: "Quantifying the Value of Packaging as a Strategy to Prevent Food Waste in America," AMERIPEEN, 2018. <http://icymodn.com/sites/www.ameripen.org/resource/freshgr/files/AMERIPEEN-WhitePaper-FoodWaste.pdf>

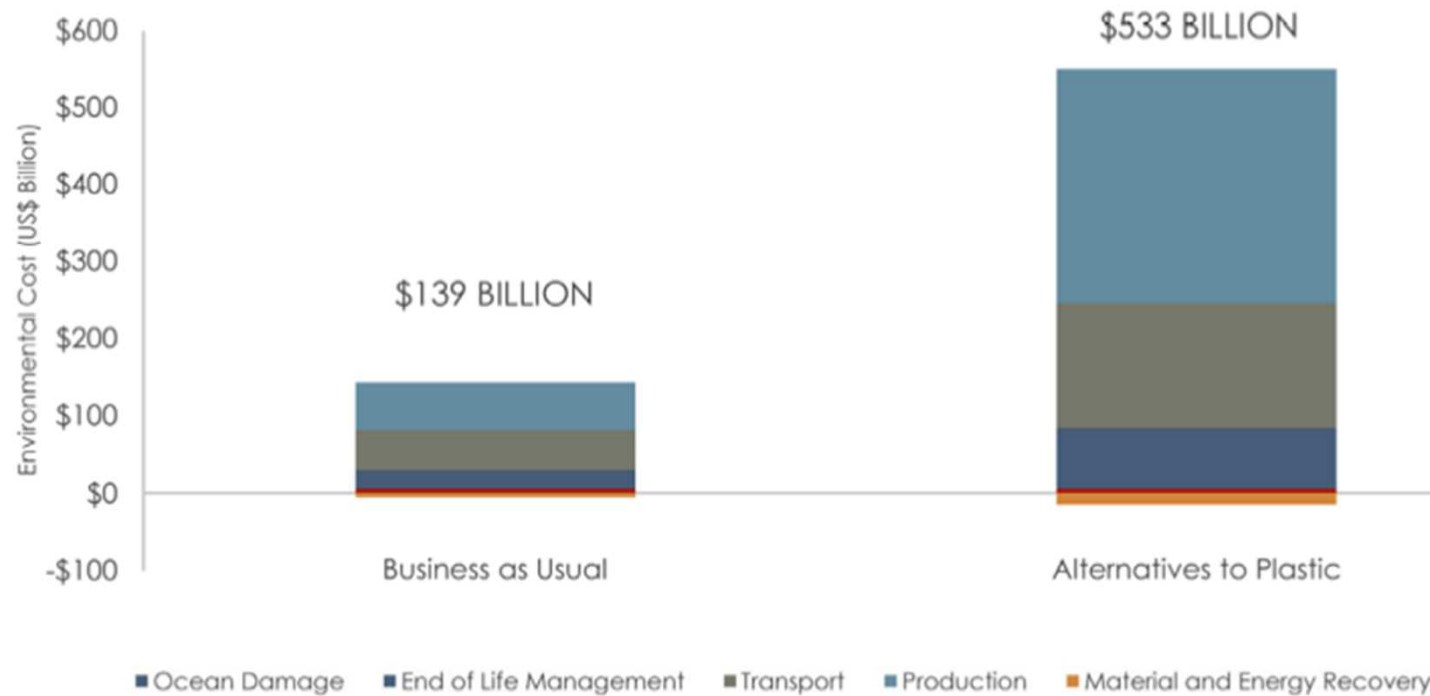
² Adapted: Euromonitor International, 2017 & ReFED 2016



Notes/Assumptions:
1. Fuel savings over 13 year operating life of gasoline and diesel passenger vehicles sold in North America in 2015.
2. Environmental cost savings include avoided life cycle water consumption, greenhouse gas and air, land and water pollutant emissions associated with fuel production, distribution and combustion.
3. Assumes 13.8 million vehicles sold in North America in 2015.

All dollar values are in USD
Source: Trucost Plastics and Sustainability: A Valuation of Environmental Benefits, Costs and Opportunities for Continuous Improvement

Environmental Costs of Plastics vs Alternatives in Consumer Goods Sector



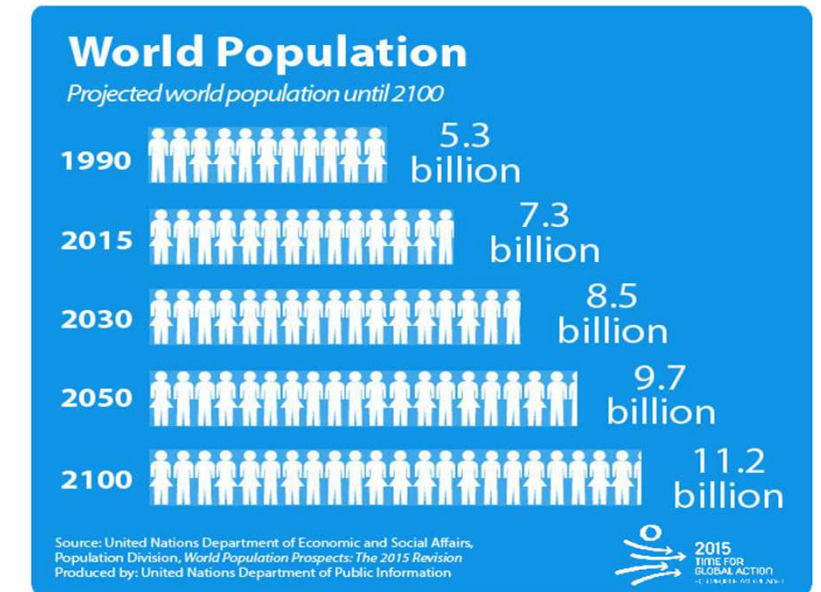
use and disposal of plastic packaging across the six studied areas per year saves:

- enough energy to fuel 18 million passenger vehicles,
- enough water to fill 461,000 Olympic swimming pools,
- waste equivalent to the weight of 290,000 Boeing 747 airplanes, and
- the acidification potential of 292,000 railcars of coal.

[Allyson Wilson](#) ACC (202) 249-6623

Food Loss and Waste

- 4 billion tons of food are produced to feed 7.6 billion people
- 30-50% of consumers are suffering from loss before reaching.
- 2 billion tons of food loss per year
- Economic losses (\$ 750 billion)
- Climate change (carbon footprint ...)
 - 3.3-5.6 billion tons of greenhouse gas
- Water reserves are depleted
 - loss of water up to the Nile River
- Loss of soil and biodiversity
 - 2 million m² area
- Time, Labor and Energy Loss



<https://www.weforum.org/agenda/2016/01/what-are-the-10-biggest-global-challenges/>



- Packaging protects food from environmental influences such as
 - heat, light,
 - presence or absence of moisture,
 - oxygen, pressure,
 - enzymes, spurious odors, microorganisms, insects, dirt and dust particles,
 - gaseous emissions, and so on
- Prolonging shelf life involves
 - retardation of enzymatic, microbial, and biochemical reactions
 - temperature control;
 - moisture control;
 - addition of chemicals
 - removal of oxygen;
 - or a combination of these with effective packaging
- Oxygen scavengers
- Carbon dioxide absorbers and emitters
- Ethylene absorbers and adsorbers
- Antimicrobials
- Moisture control agents
- Temperature control: self-heating and cooling (PCM)
- Flavor and odor absorbers
- High chemical barrier material innovations
- Sustainable food packaging

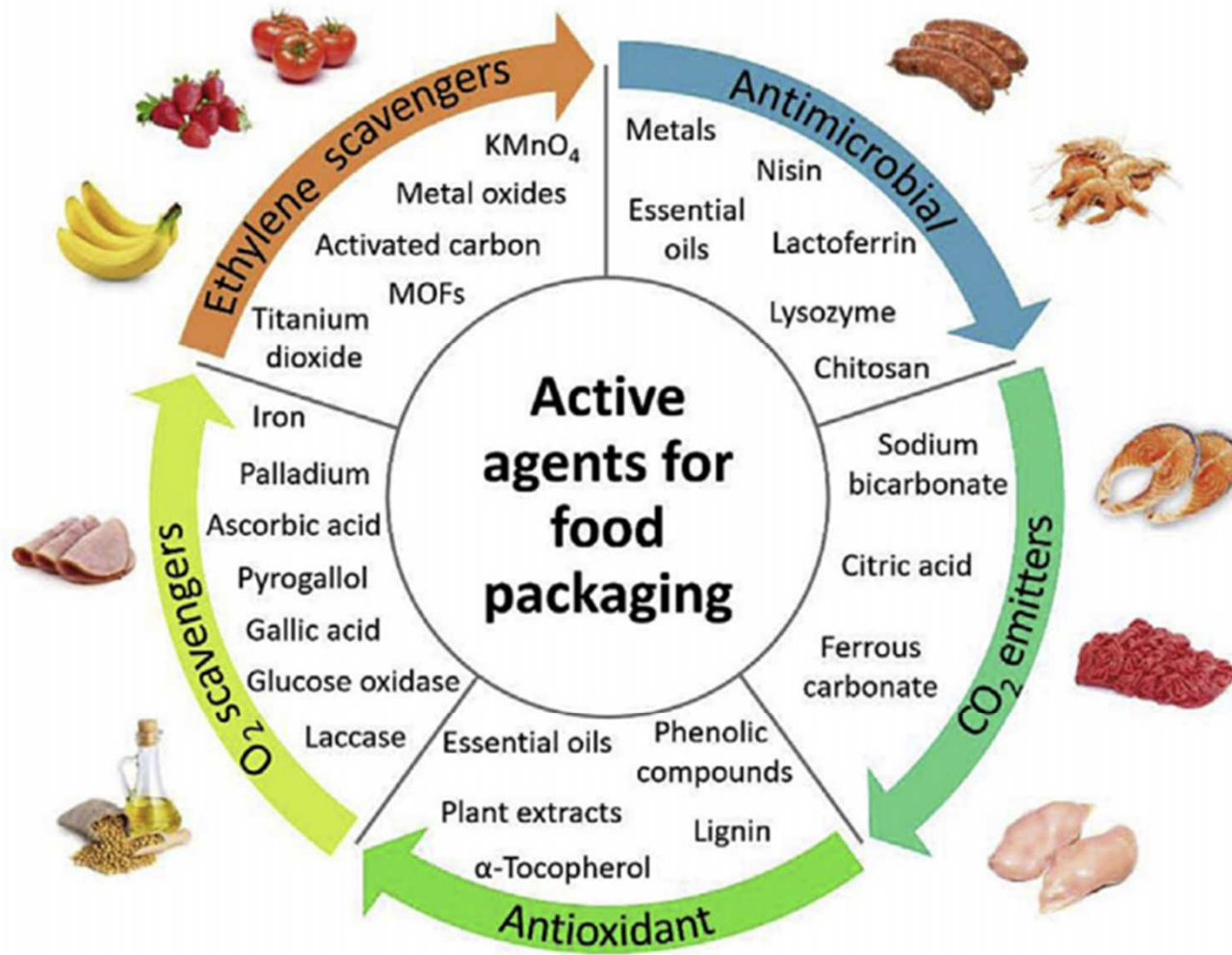
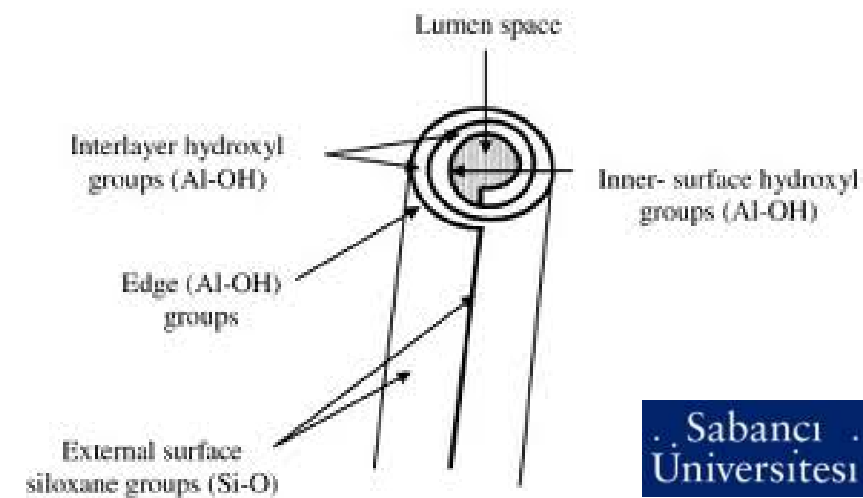
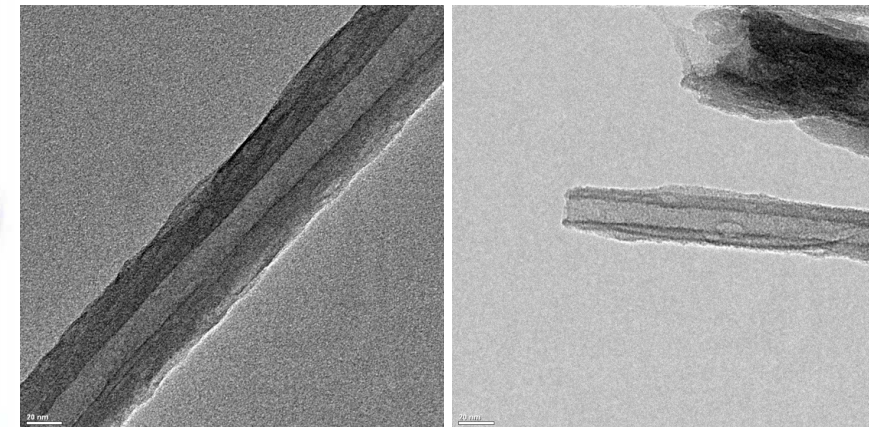


Fig. 2. Active agents for active food packaging.

Trends in Food Science & Technology 80 (2018) 212–222

Nanotechnology has the potential to transform food packaging



Composite

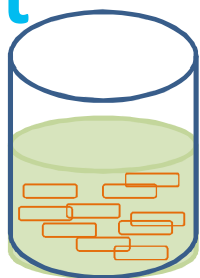
HNTs are nanotubes with high L/D ratio and possess a low density of surface hydroxyl groups compared with other silicates. Consequently it is expected that HNTs will be promising as reinforcing fillers for polymer materials

- Multiple Function
 - Mechanical (strength and modulus)
 - Antimicrobial
 - Absorbent
 - Antistatic
 - Barrier
 - Thermal balance
- Light Weight
- Low Gauge

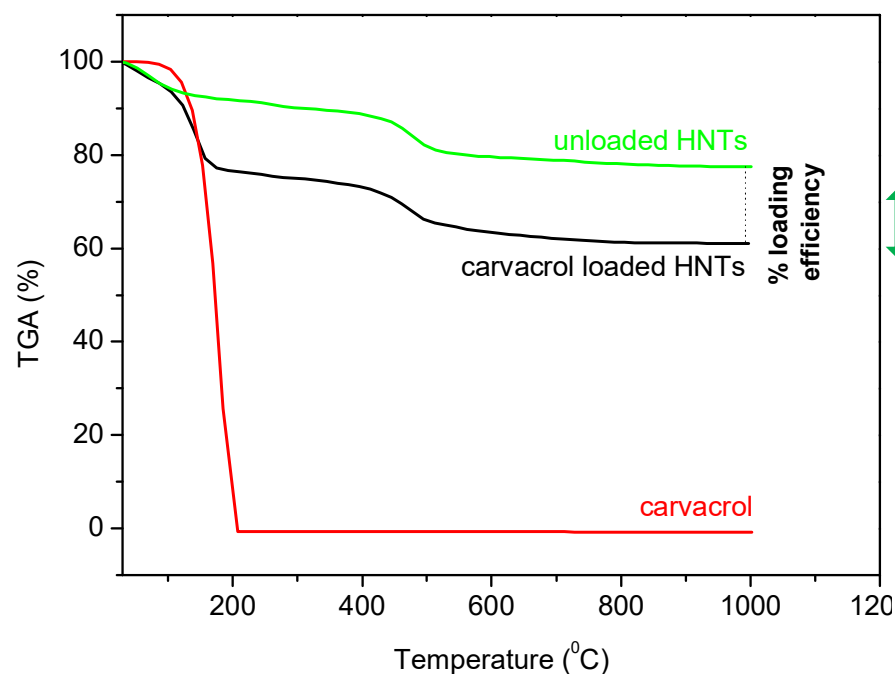
Responsible Consumption and Production

Carvacrol Loaded Halloysite Nanotubes, as Antimicrobial and Antioxidant

Carvacrol/HNT mixture



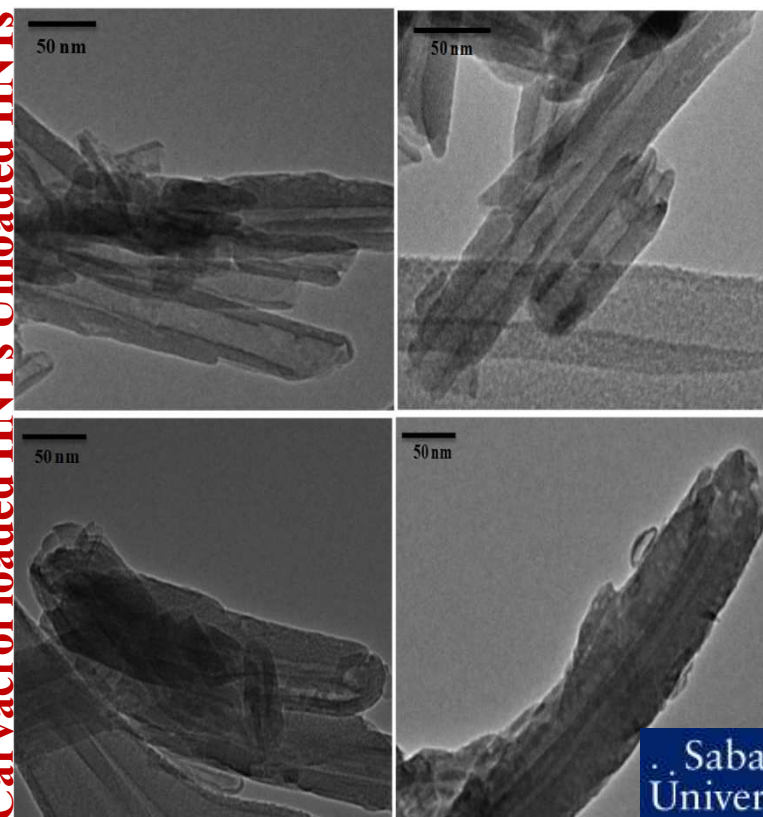
- 1) Ultrasonication
- 2) Vacuum application
- 3) Removing excess carvacrol
- 4) Washing to remove surface adsorbed carvacrol
- 5) Drying into powder



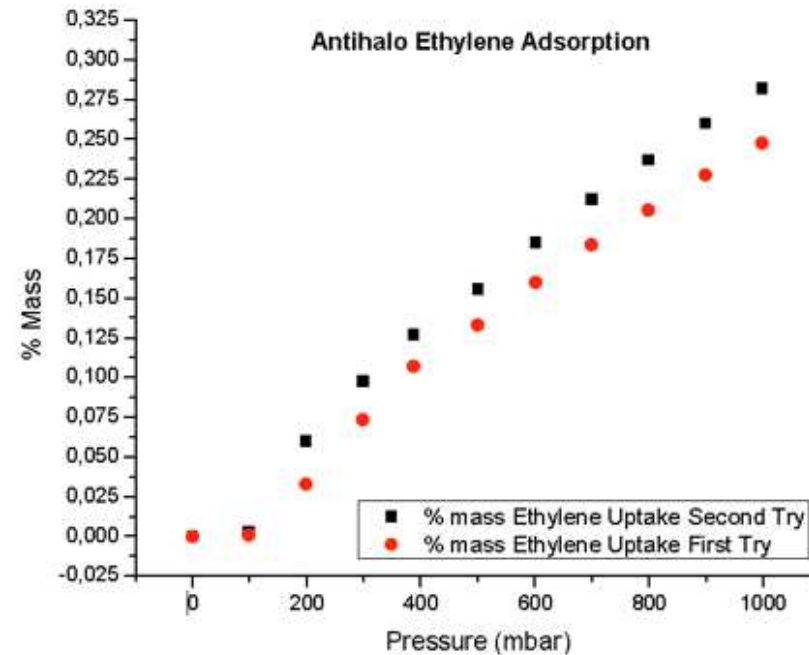
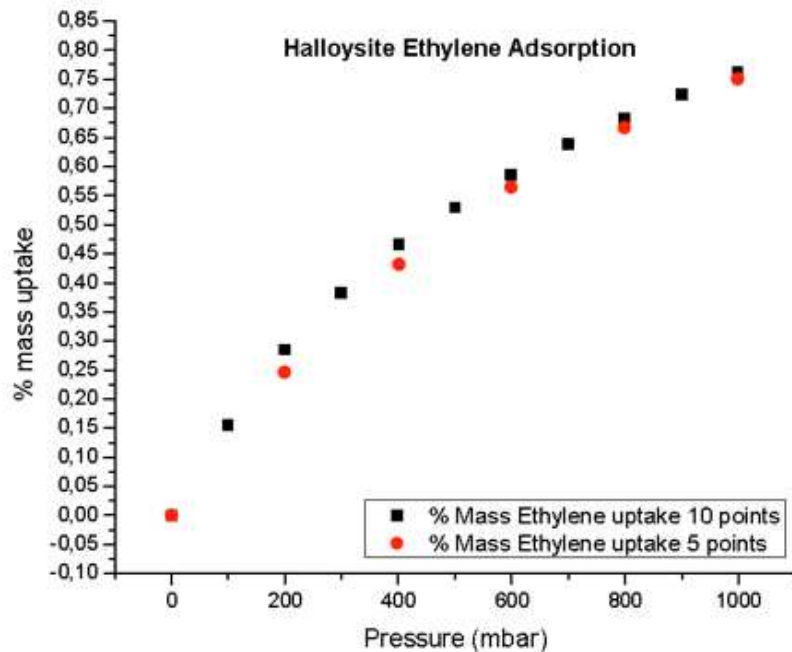
Ünal *et al.*, Progress in Organic Coatings, 2016, 101, 253-261.

17.40 ± 3.05 %

Carvacrol loaded HNTs Unloaded HNTs



Ethylene adsorption capacity of Halloysite Nanotubes



Halloysite adsorption experiments were performed by using Hiden Isochema Intelligent Gravimetric analyzer (IGA-003) with ethylene gas

Regular Ethylene scavengers capacity is around 2500 microliter/g, functionalized HNT varies between 3000-8000 microliter/g

PCMs are passive thermal energy storage materials used in the thermal packaging industry to maintain a temperature-sensitive product within the manufacturer's required temperature range during all transportation phases

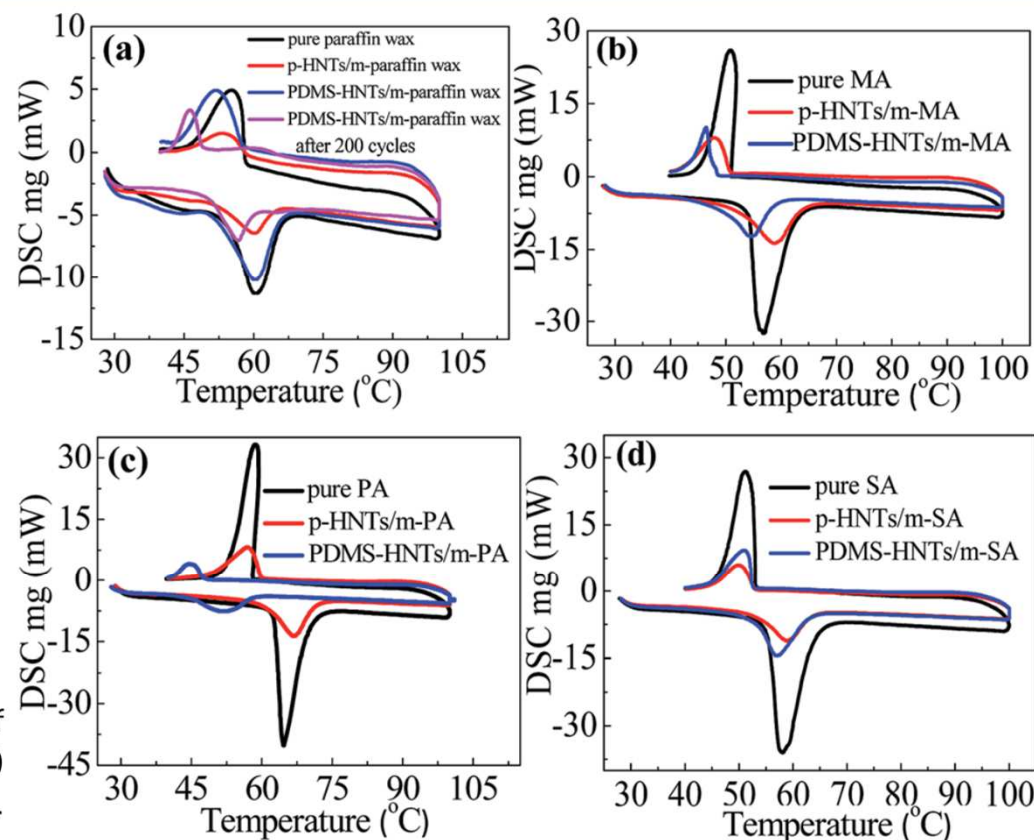
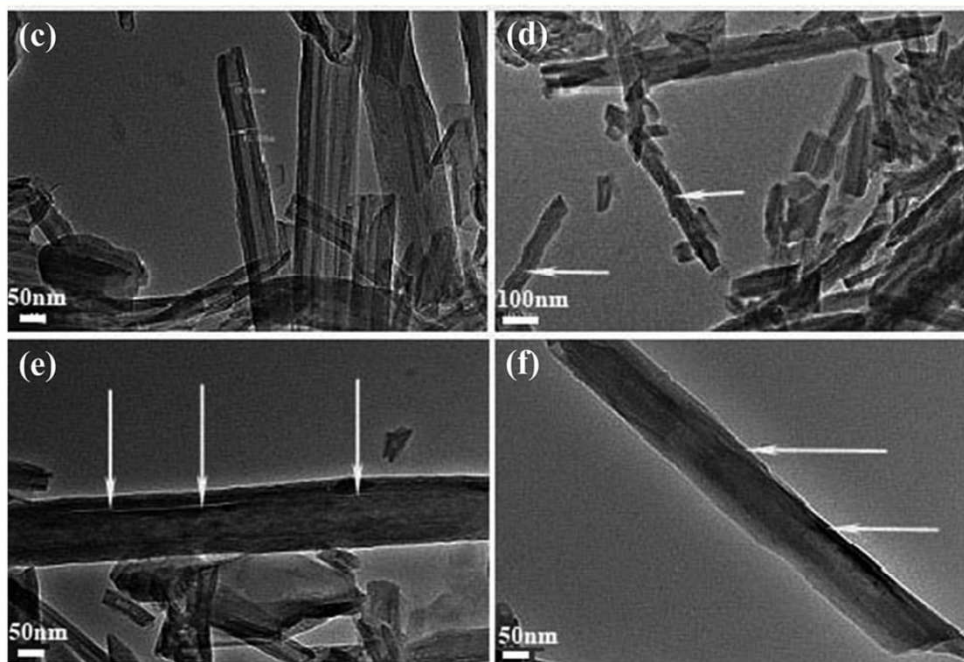
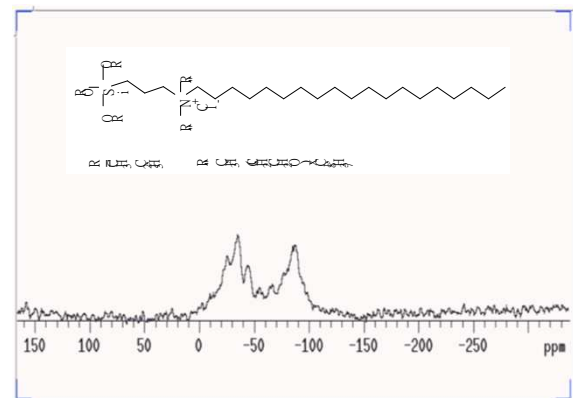
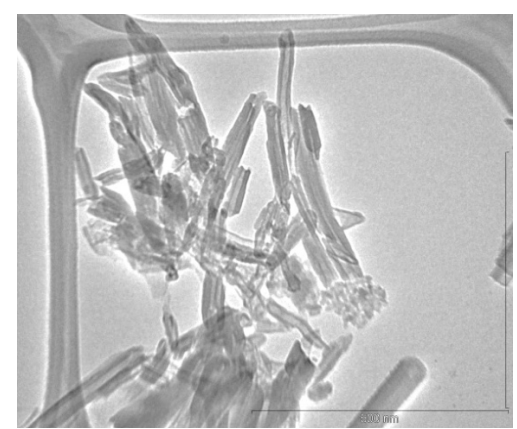
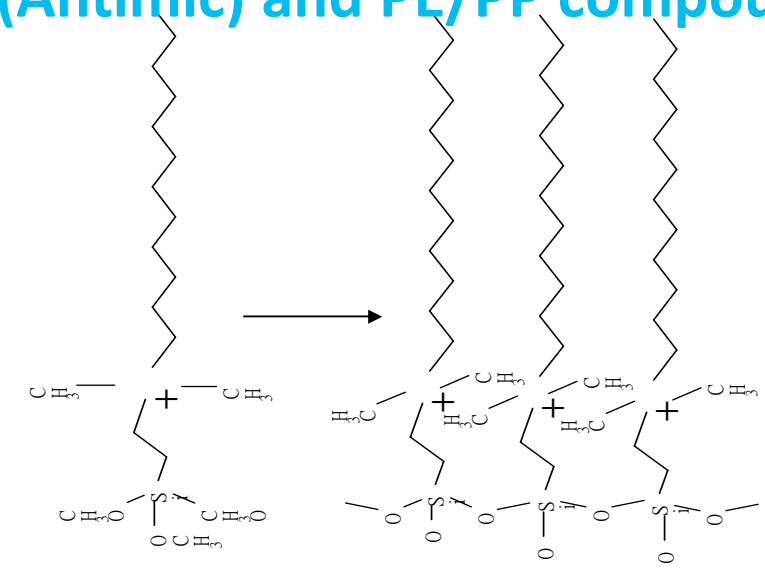


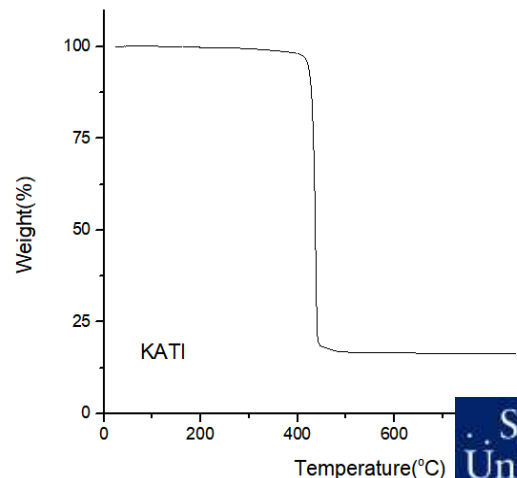
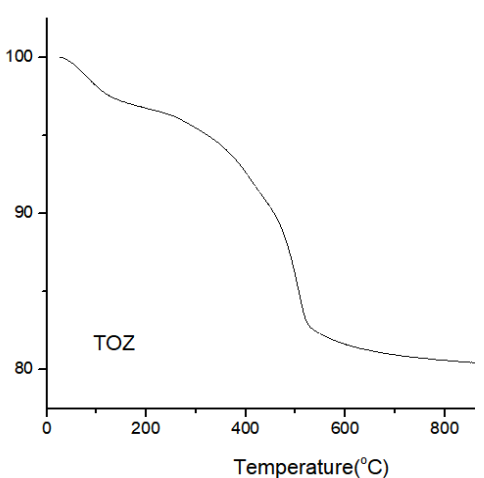
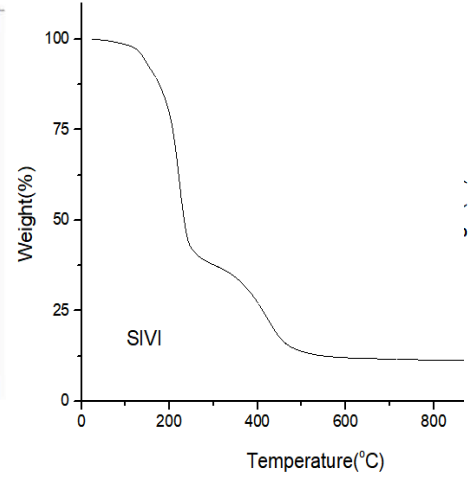
Fig. 1 SEM images of (a) p-HNTs and (b) PDMS-HNTs. TEM images of (c) PDMS-HNTs, (d) PDMS-HNTs/m-paraffin wax composite, (e) PDMS-HNTs/m-MA composite and (f) PDMS-HNTs/v-MA composite. Scale bar: (a, b, d) 100 nm and (c, e, f) 50 nm.

Energy removal to lower [1kg] of liquid water from (+5°C) to (+2°C) = 12.6 kJ x 20=240
 Energy removal to lower [1kg] of liquid PCM (+5°C) to frozen PCM (+2°C) = 233.3 kJ

HNT coated w [3-(trimethoxysilyl)-propyl, alkyldimethylammonium chloride] (Antimic) and PE/PP compound



Si²⁹-NMR (Single Pulse-MAS)



Antimic-Powder PE Nanocomposite Film Preparation and Properties

- 20 % wt Antimicrobial powder used for Masterbatch preparations
- 1, 3, 4, 5 % wt masterbatch used for polyethylene blown/cast film production
- Polypropylene-injection molding
- Polyurethane-coatings and injection molding
- Polyamide-injection molding and film
- Polyesters-blown molding, injection molding, film etc...

Mechanical properties of PE film w Antimic coated HNT Powder

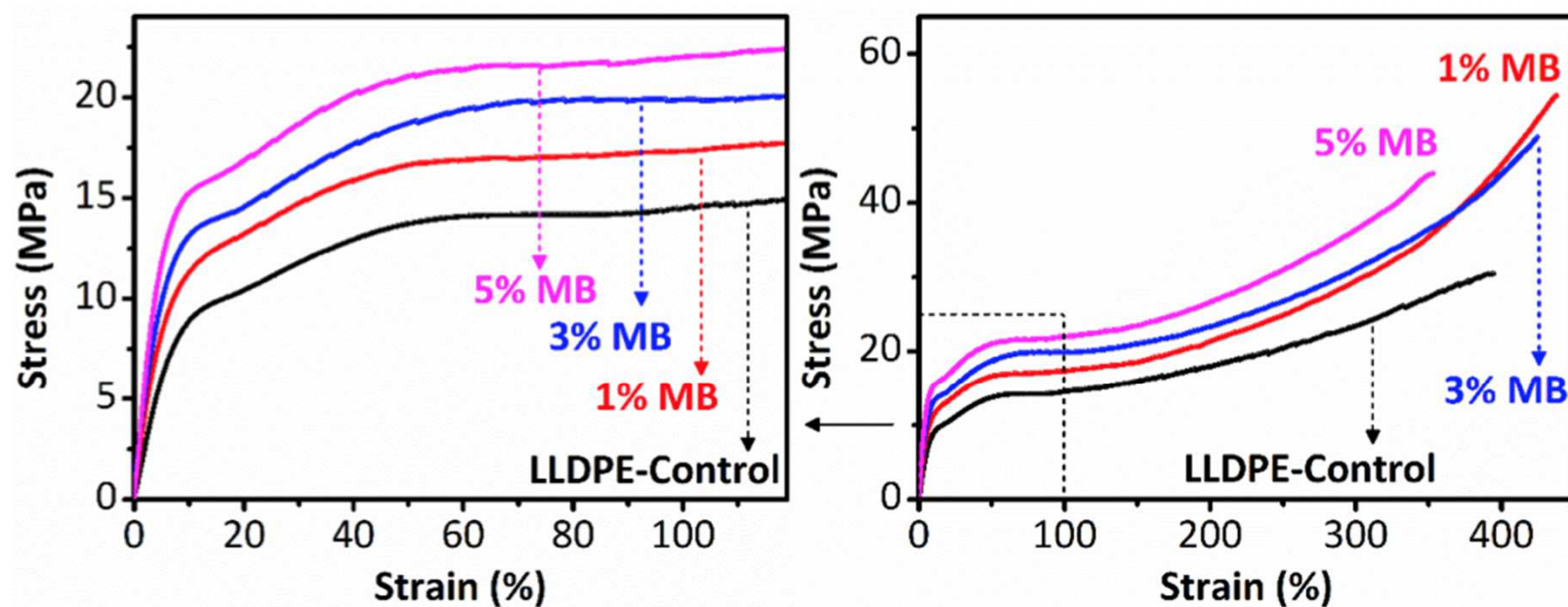


Figure 2. Stress-strain curves of LLDPE/MB film samples (right) along with expanded linear region (left).

% Increase Mechanical Properties Machine and Transverse Direction

Mechanical properties of LLDPE/MB film samples (machine direction)

Sample	E (MPa)	$\sigma_{100\% \text{ strain}}$ (MPa)	σ_{\max} (MPa)	ϵ (%)	W (MJm ⁻³)
LLDPE-Control	109±8	14.5±0.7	30.4±1.9	390±20	75±7
1% MB	243±6	17.3±0.4	54.4±2.1	440±10	114±6
3% MB	277±13	19.9±0.6	48.8±1.7	420±10	113±9
5% MB	312±11	22.0±0.7	43.9±1.2	350±10	95±8

Mechanical properties of LLDPE/MB film samples (transverse direction)

Sample	E (MPa)	$\sigma_{100\% \text{ strain}}$ (MPa)	σ_{\max} (MPa)	ϵ (%)	W (MJm ⁻³)
LLDPE-Control	125±22	9.01±0.3	15.6±2.9	407±104	46±12
1% MB	144.6±27	8.27±0.2	10.6±1.6	275±40	25±6
3% MB	166.4±40	8.27±0.1	9.87±2.5	281±131	27±17
5% MB	172.6±11	8.47±0.1	10.0±0.9	292±21	28±3

Antimicrobial Performance of PE film w Antimic Powder- JIS Z 2801:200 method

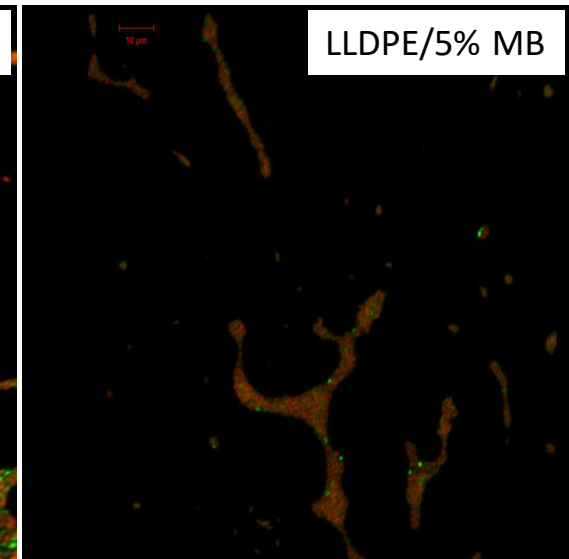
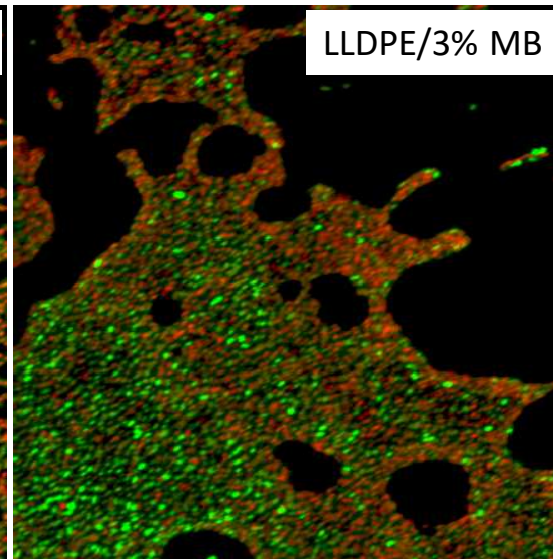
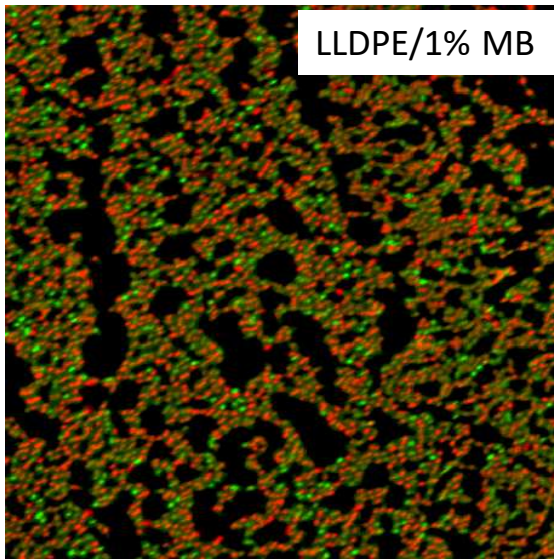
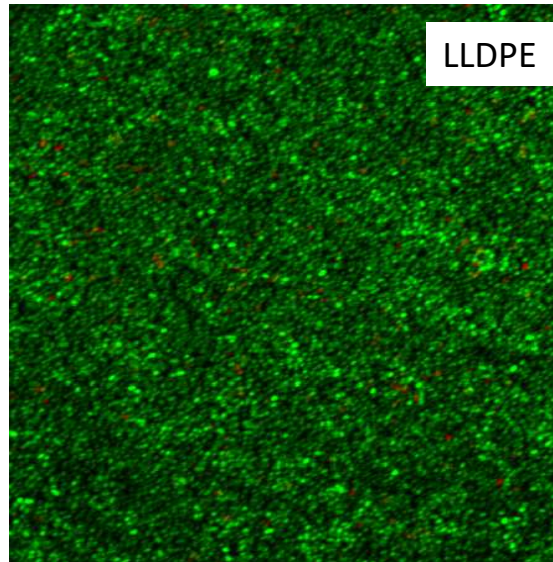
S. Aureus

Örnek	<i>S. aureus</i> ATCC 6538	% Öldürme Oranı	R değeri
	Mikrobiyal yük *kob/ml		
24.saat	24.saat	24.saat	24.saat
% 1 MB Uygulanmış Malzeme	1.25x10 ²	99.967	3.49
	1.00x10 ²	99.974	3.59
	0.8x10 ²	99.979	3.68
% 3 MB Uygulanmış Malzeme	7.5x10	99.980	3.71
	50	99.987	3.89
	1.20x10 ²	99.969	3.51
% 5 MB Uygulanmış Malzeme	1.10x10 ²	99.971	3.54
	9.90x10 ²	99.746	2.59
	5.78x10 ³	98.517	1.82
Kontrol	2.70x10 ⁵ (0. Saat)	—	—
	3.90x10 ⁵ (24. Saat)		
Bakteri Kontrol	2.0x10 ⁵		

E. Coli

Örnek	<i>E. coli</i> ATCC 8739	% Öldürme Oranı	R değeri
	Mikrobiyal yük *kob/ml		
24.saat	24.saat	24.saat	
% 1 MB Uygulanmış Malzeme	1.24 x10 ⁴	99.436	2.24
	2.77x10 ³	99.874	2.89
	6.65x10 ³	99.697	2.51
% 3 MB Uygulanmış Malzeme	1.01x10 ³	99.954	3.33
	2x10 ³	99.909	3.04
	7x10 ²	99.968	3.49
% 5 MB Uygulanmış Malzeme	2.13x10 ⁵	99.318	1.01
	1.30x10 ⁴	99.409	2.22
	2.10x10 ⁴	99.045	2.02
Kontrol	5.41x10 ⁵ (0. Saat)	—	—
	2.20x10 ⁶ (24. Saat)		
Bakteri Kontrol	4.0x10 ⁵		

Films incubated with *Pseudomonas aeruginosa* for 48 h



Controlled Release

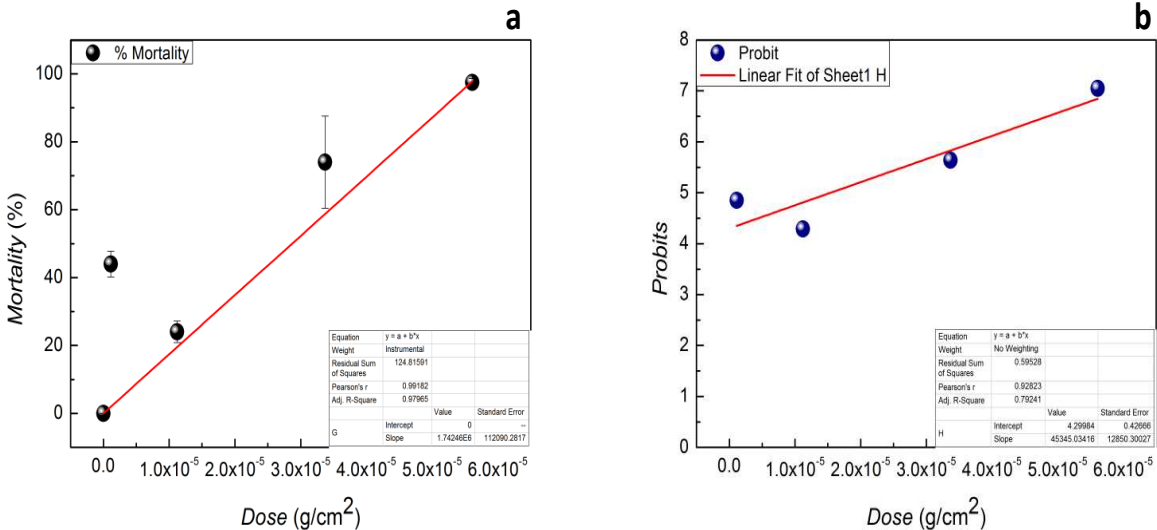
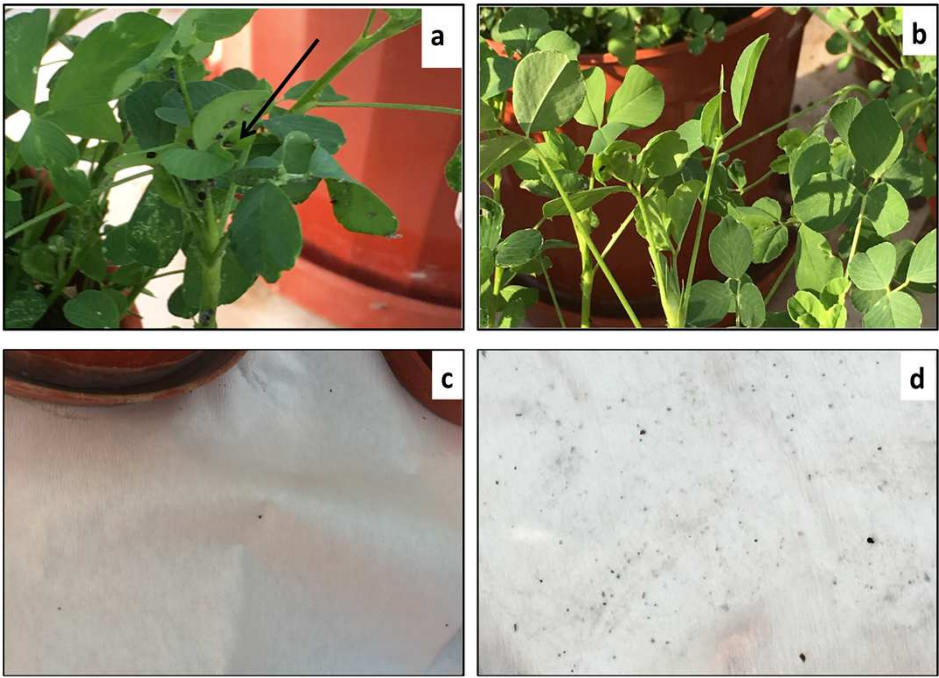
As the lumens of HNTs could be loaded with drugs or other chemicals, HNTs are expected to be ideal materials for controlled or sustained release of drugs, other bioactive molecules or other additives

Food security and Sustainable agriculture

- Antifouling
- Antibacterial
- Antifungal
- Pesticides

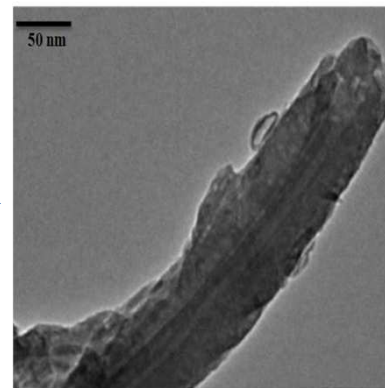
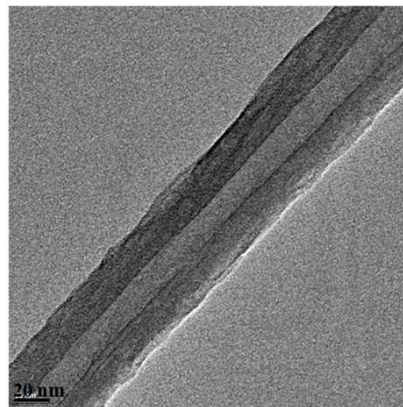
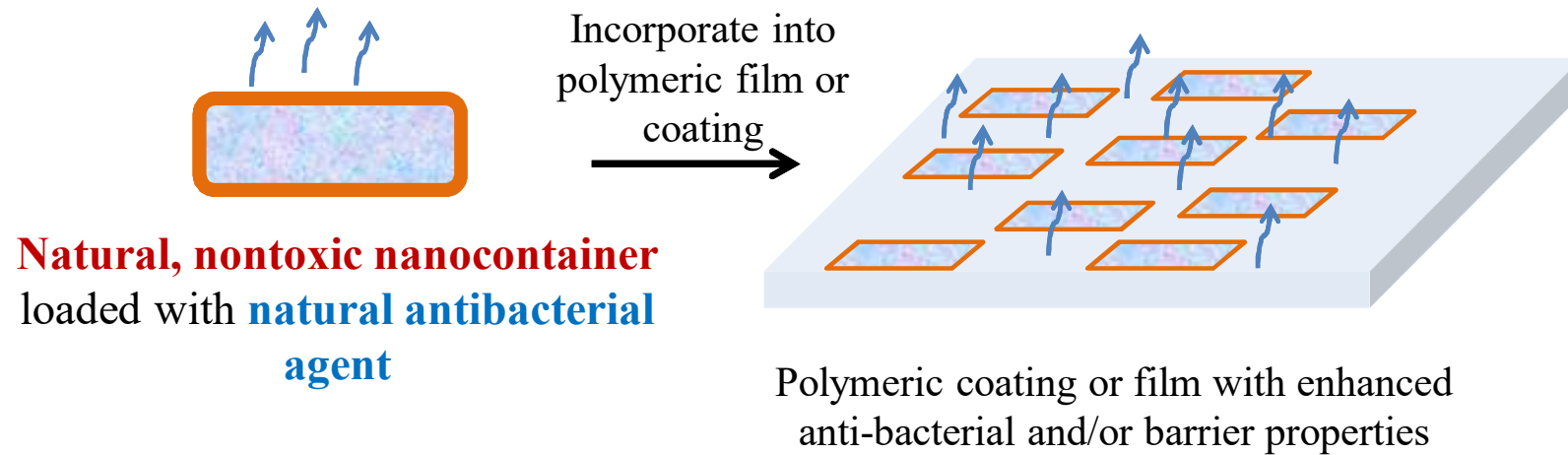
Zero Hunger

There are 600,000 da greenhouse, 200,000 da low tunnel cultivation of it,
 Total of 7 million tons of vegetable production, 1/3 low tunnel production
 10 kg of pesticides are used per da means 2 tons of pesticides and 0.1% of it
 reaches the target,
 Approx 60,000 tons of greenhouse cover film needed 0.3-1% insecticide
 loaded HNT sufficient

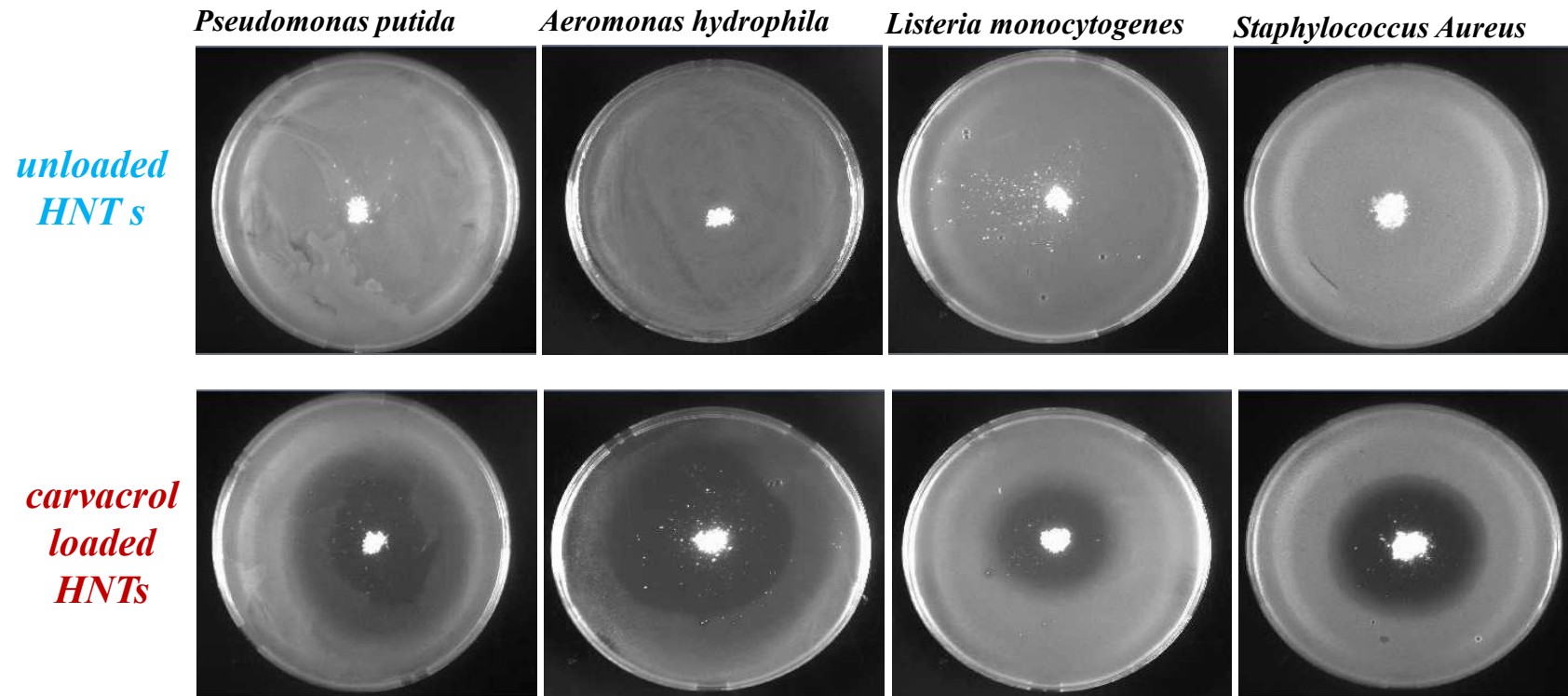


(a) Insect mortality graph, (b) Probit line responses. % values represent mortality levels that are transformed to probit for statistical analysis.

Multi-Functional Polymeric Nanocomposites using Halloysite Nanotubes



Antibacterial Activity of Carvacrol Loaded HNTs



Antimicrobial Performance of PE film w Carvacrol Powder-JIS Z 2801:200 method

S. Aureus

Örnek	<i>S. aureus</i> ATCC 6538	% Öldürme Oranı	R değeri
	Mikrobiyal yük *kob/ml		
Örnek	24.saat	24.saat	24.saat
% 2 Carvacrol Uygulanmış Malzeme	< 10	99.997	4.59
	< 10	99.997	4.59
	< 10	99.997	4.59
% 5 Carvacrol Uygulanmış Malzeme	6.15x10 ³	98.423	1.80
	< 10	99.997	4.59
	2.40x10 ²	99.938	3.21
% 10 Carvacrol Uygulanmış Malzeme	< 10	99.997	4.59
	< 10	99.997	4.59
	< 10	99.997	4.59
% 25 Carvacrol Uygulanmış Malzeme	9.50x10 ²	99.756	2.61
	7x10	99.982	3.74
	8x10	99.979	3.68
Kontrol	2.70x10 ³ (0. Saat)	—	—
	3.90x10 ³ (24. Saat)		
Bakteri Kontrol	2.0x10 ³		

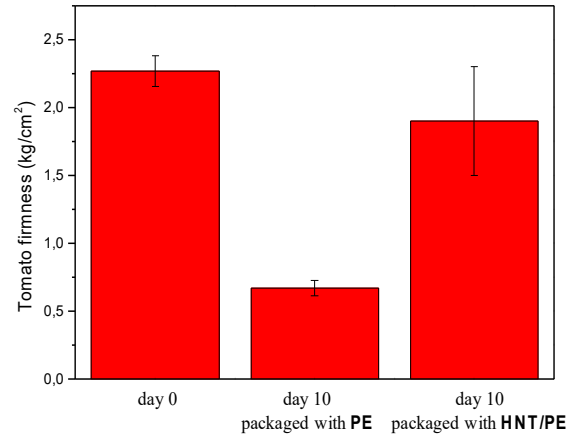
E. Coli

Örnek	<i>E. coli</i> ATCC 8739	% Öldürme Oranı	R değeri
	Mikrobiyal yük *kob/ml		
	24.saat	24.saat	24.saat
% 2 Carvacrol Uygulanmış Malzeme	1.20 x10 ³	99.945	3.26
	4.0x10	99.998	4.74
	4.45x10 ²	99.979	3.69
% 5 Carvacrol Uygulanmış Malzeme	2.80x10 ³	99.872	2.89
	2.33x10 ⁴	98.940	1.97
	3.5x10 ²	99.984	3.79
% 10 Carvacrol Uygulanmış Malzeme	< 10	99.999	5.34
	< 10	99.999	5.34
	< 10	99.999	5.34
% 25 Carvacrol Uygulanmış Malzeme	1.40x10 ⁵	93.636	1.19
	1.35x10 ³	99.938	3.21
	1.00x10 ³	99.954	3.34
Kontrol	5.41x10 ⁵ (0. Saat)	—	—
	2.20x10 ⁶ (24. Saat)		
Bakteri Kontrol	4.0x10 ⁵		

A)



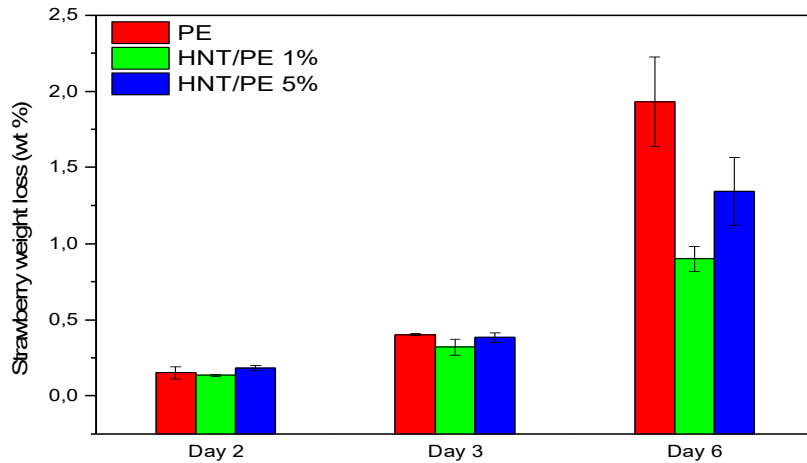
B)



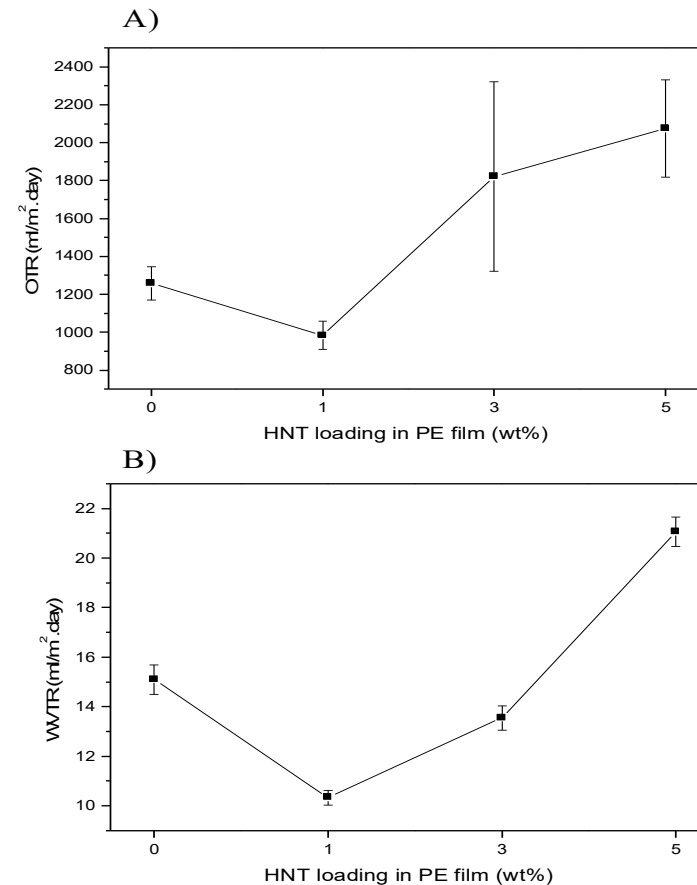
Photographs of banana samples packaged with PE films and HNT/PE films containing 5 wt % HNTs B) Firmness of tomato samples packaged with PE films and HNT/PE films containing 5% HNTs.



By Courtesy of Dr. Hayriye Ünal-SUNUM



Time based weight loss of strawberries packaged with neat PE films (red), nanocomposite films loaded with 1 wt % (green) and with 5 wt % HNTs (blue).



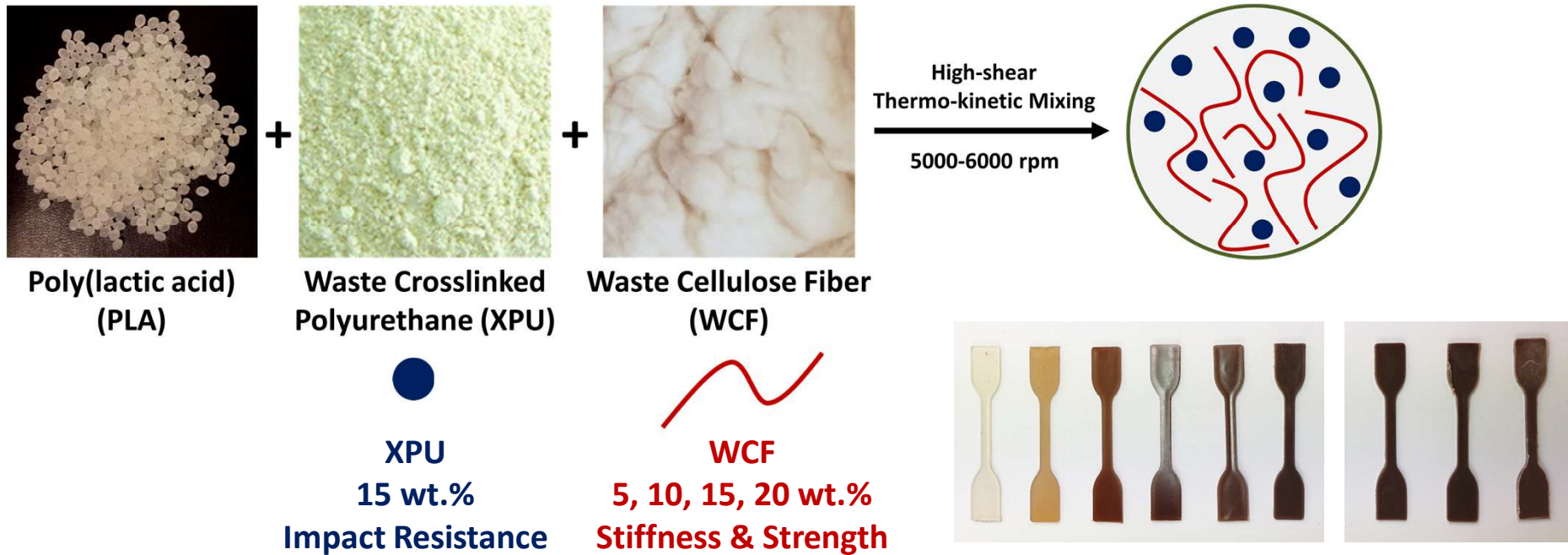
Oxygen transmission rate (OTR) (A) and water vapor transmission rate (WVTR) (B) of nanocomposite films at different loading ratios.

UPCYCLING

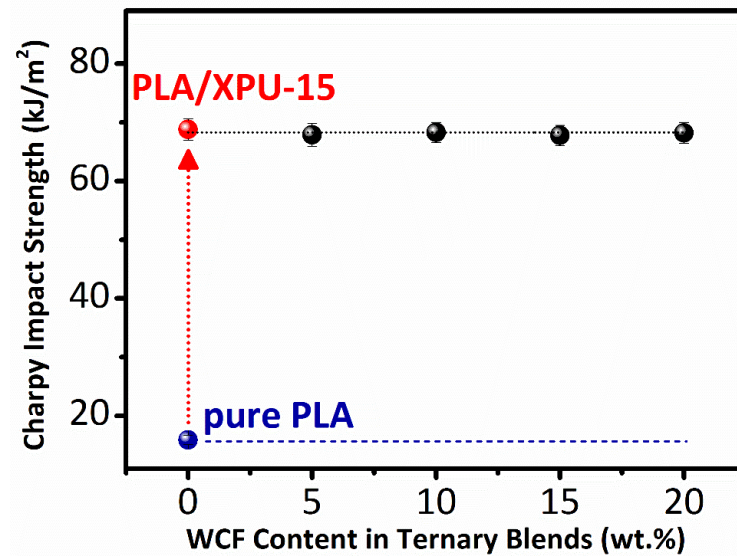
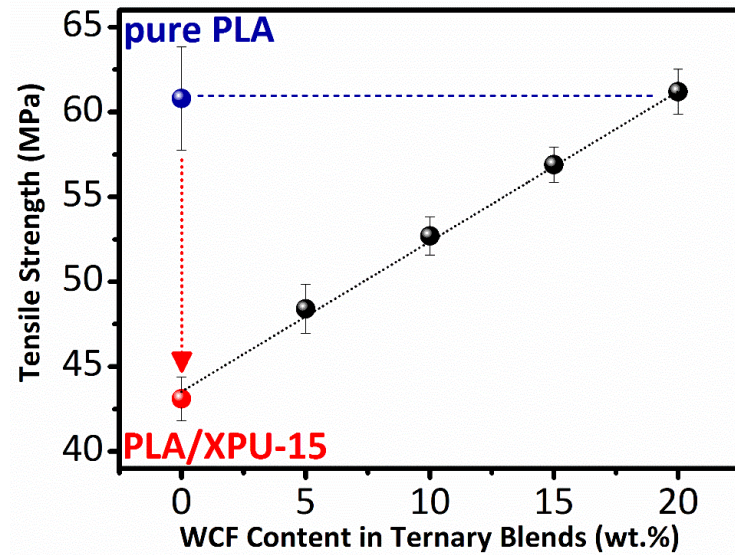
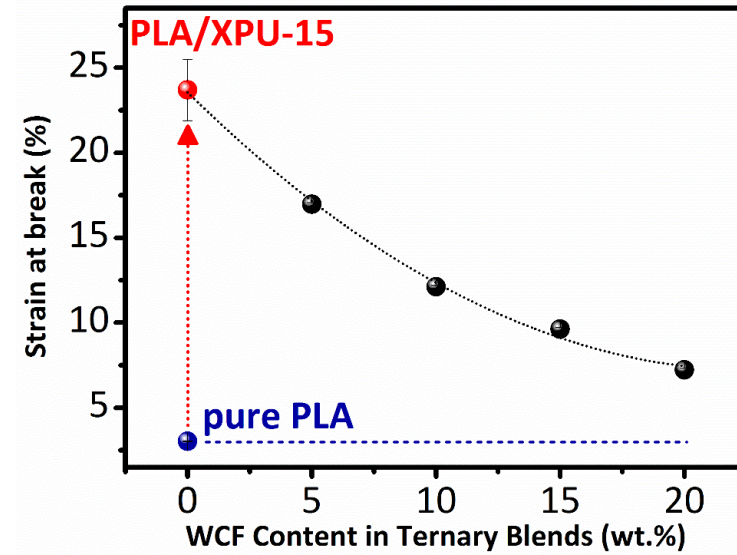
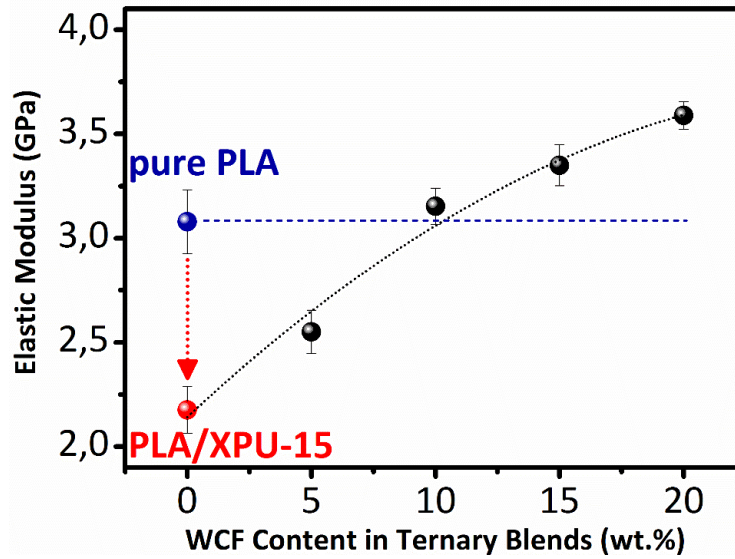
PLA/XPU/WCF TERNARY BLENDS

65% increase in stiffness, 42% increase in strength by using 15% waste cellulose fiber and waste vulkollan

PLA/XPU/WCF Ternary Blends



Ternary Blends: Mechanical Properties



Plastics recycling with a difference

by Haritz Sardon, and Andrew P. Dove

Science
Volume 360(6387):380-381
April 27, 2018

Published by AAAS

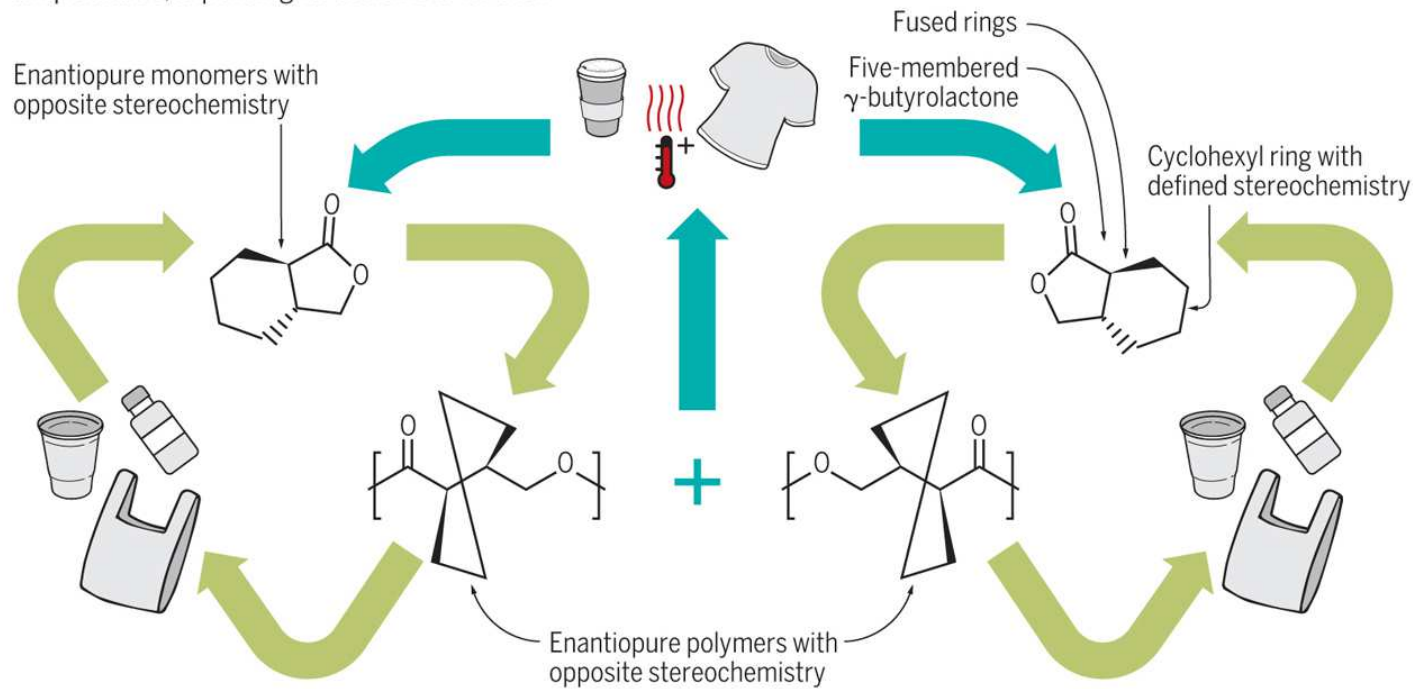


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Repeatedly recyclable polymers

Repeatedly recyclable polymers

Zhu *et al.* report production of a plastic that can be recycled repeatedly through chemical methods without loss of function. Blending of the two enantiopure polymers yields a plastic that can withstand higher temperatures, expanding its usefulness further.



Haritz Sardon, and Andrew P. Dove *Science* 2018;360:380-381

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Bibliographic data: SG184970 (A1) — 2012-11-29

PREPARATION OF SUBSTANTIALLY QUATERNIZED AMMONIUM ORGANOSILANE COMPOSITION AND SELF-STABILIZING AQUEOUS SOLUTION THEREOF

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Classification: - international: C07F7/1892
- cooperative:

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Abstract of SG184970 (A1)

This invention relates to the preparation of a partially quaternized ammonium organosilane composition, and a self-stabilizing aqueous solution of said composition, which serves to yield an antimicrobial polysilsesquioxane coating upon thermal curing. By way of this invention, an aqueous solution is prepared, comprised in part by a partially

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Description

Claims

Abstract

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(54) Food packaging material with antibacterial, ethylene scavenging and barrier properties

(57) The present invention provides an use of polymeric films comprising halloysite nanotubes as a packaging material for food products. Said halloysite nanotubes are incorporated with active agents such as anti-

bacterial agents preferably of natural type for providing antibacterial, barrier and ethylene scavenging properties.

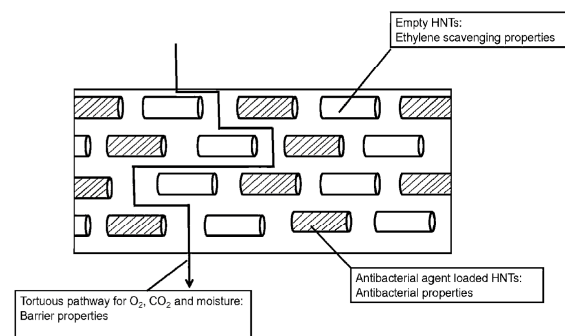


Fig. 4

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