Ageing of Petroleum- and Biobased Polymers, from Nuclear Power Plants to Packaging Materials

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Ca. 130 people

A major part: PhD students

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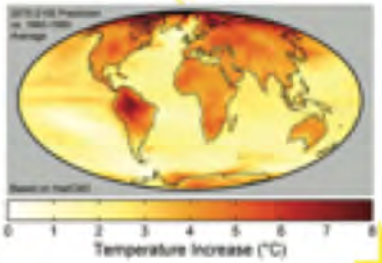
Energy hunger

Global warming



Food

Water

Polymeric Materials

Source limitations

Health

Long-term properties
Life-time prediction, Accelerated ageing

oxidation, hydrolysis, depolymerization, DLO, migration, swelling, physical ageing, vitrification

- Plastic pipes/tubes (gas, oil, fuel, water)
- Cables and seals (air, water) - Nuclear power plants
- Quick connectors (fuel)
- Polymer films
- Cables – electric transmission

Nuclear Power Plants

47 % EPDM
39 % carbon black
5 % $CaCO_3$
6-7 % paraffine oil
1 % S
….

30 % EPDM
6 % $CaCO_3$
35 % $Al(OH)_3$
6-7 % stearine/waxes
2 % S
……

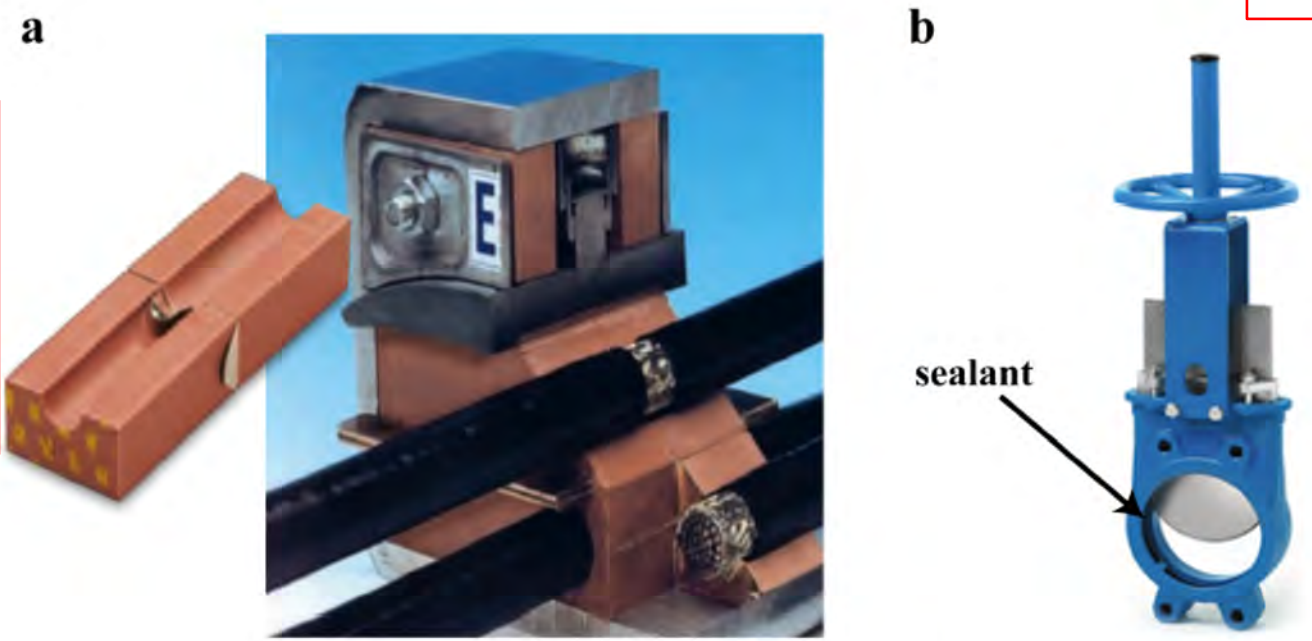
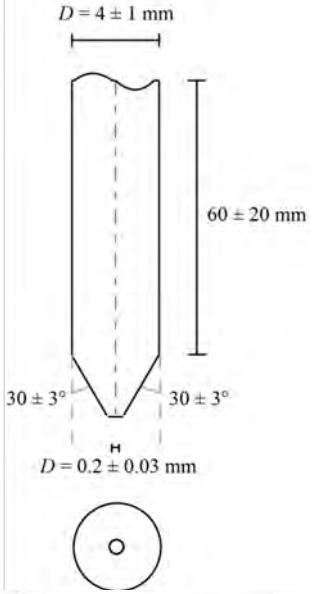
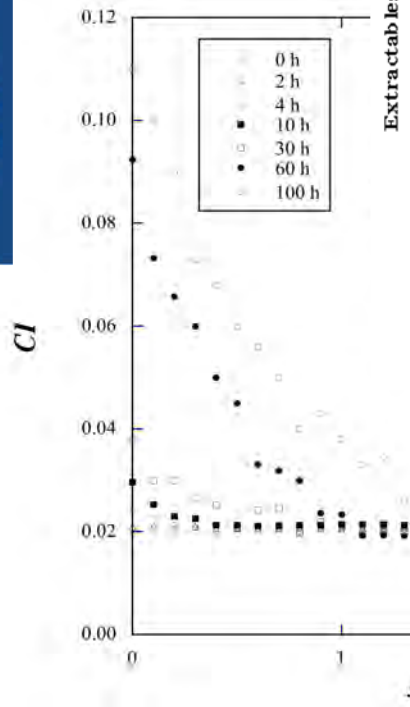


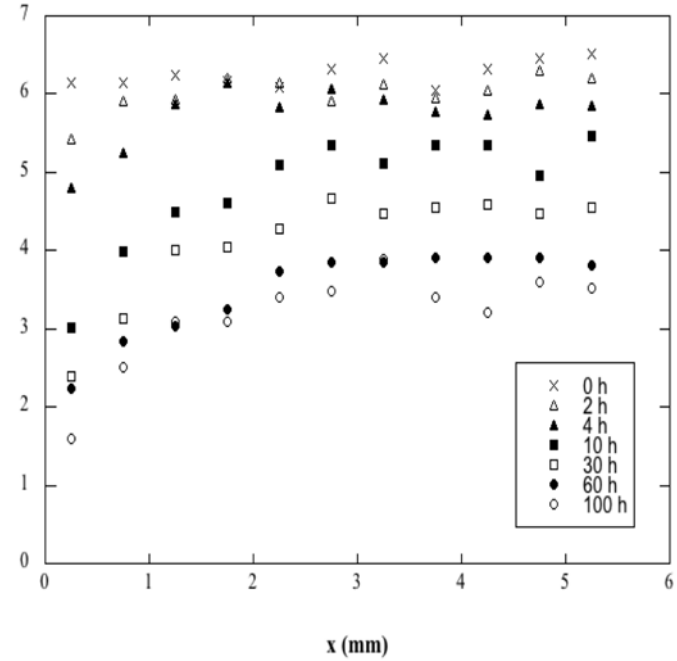
Fig. 1 a) A cross-section of a cable transit system. Lycron seal blocks (pink) can be seen packed in the frame structure. b) Carbon black-containing EPDM seal installed in a transportation valve (knife-port valve).

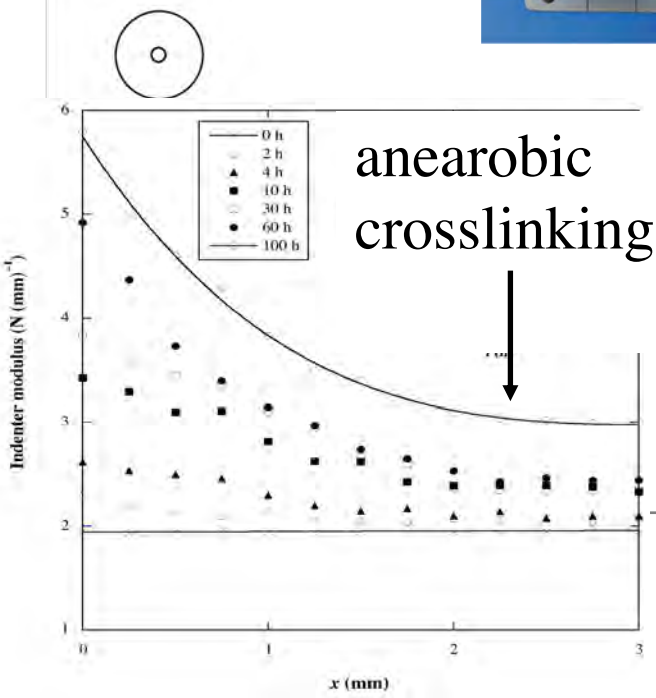
Profiling of thermally aged EPDM seals using portable NMR, indenter measurements and IR spectroscopy facilitating separation of different deterioration mechanisms



Oxidation, anearobic crosslinking and loss of oil extender (170 C)







anearobic crosslinking

P. Pourmand, E. Linde, M. Hedenqvist, I. Furo, S.V. Dvinskikh, U. W. Gedde, *Polym. Test.* **53** (2016) 77-84.

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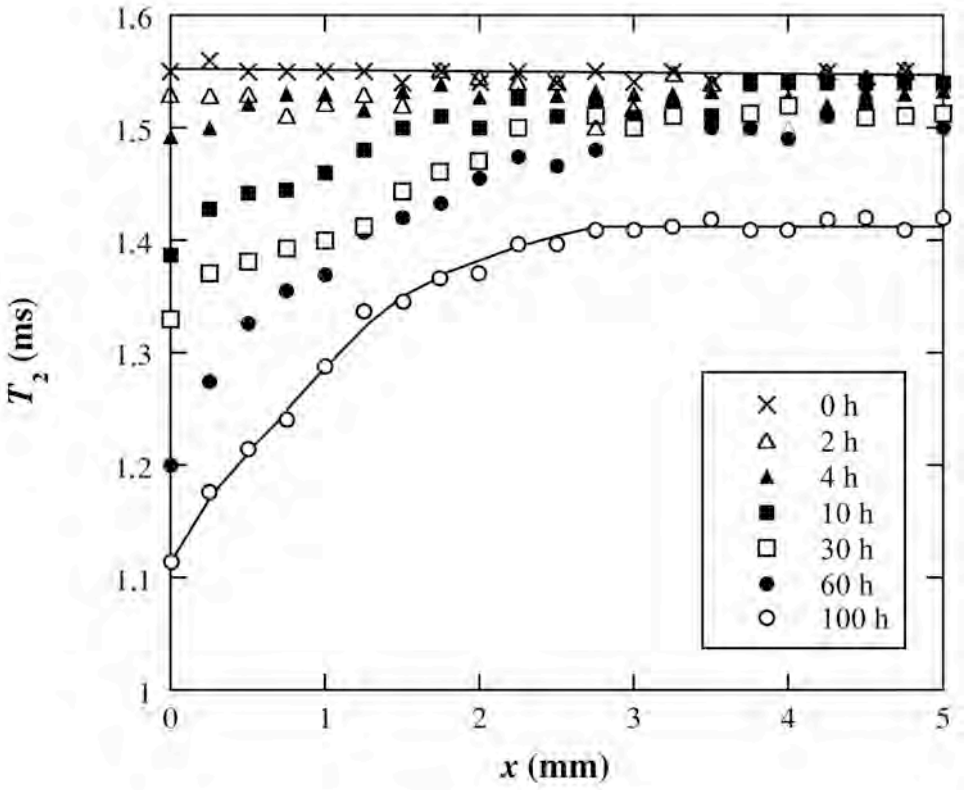
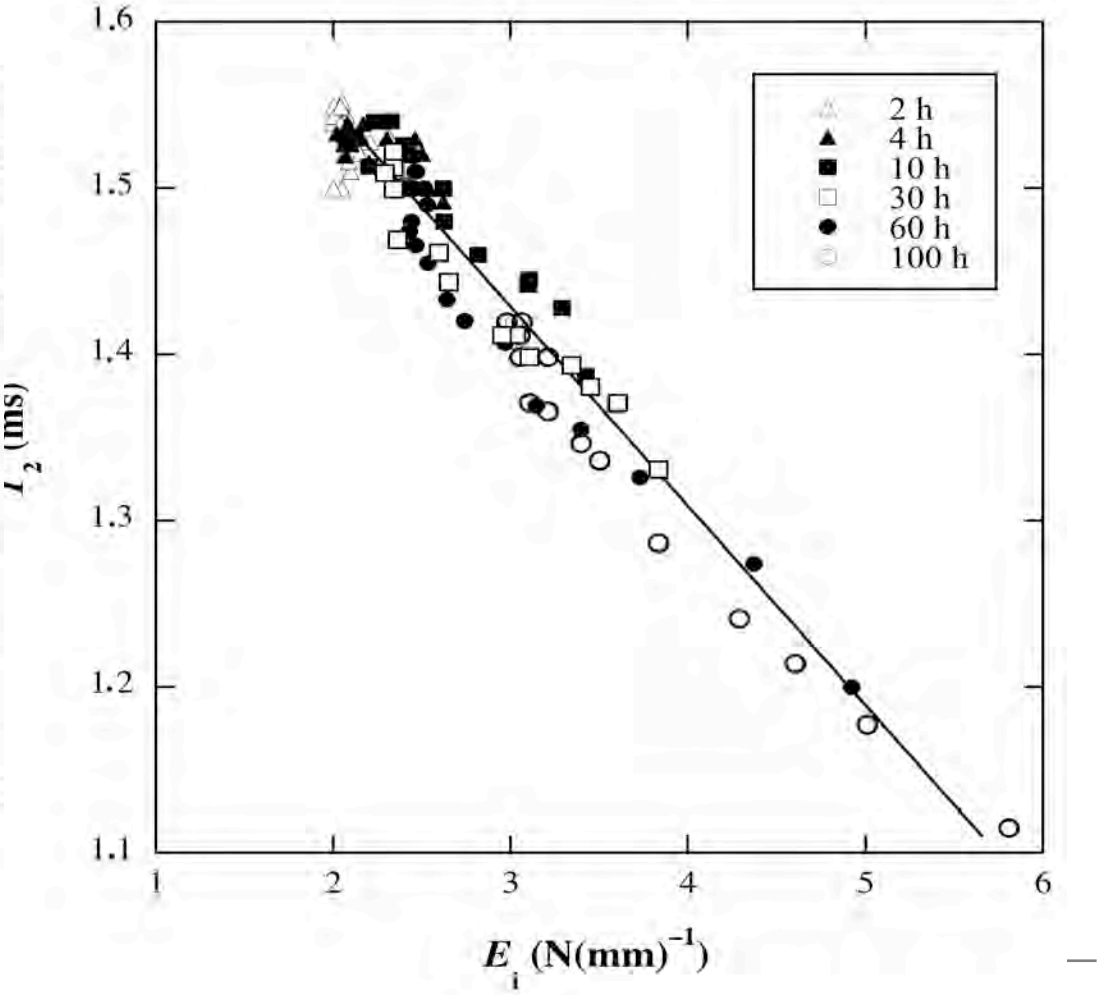
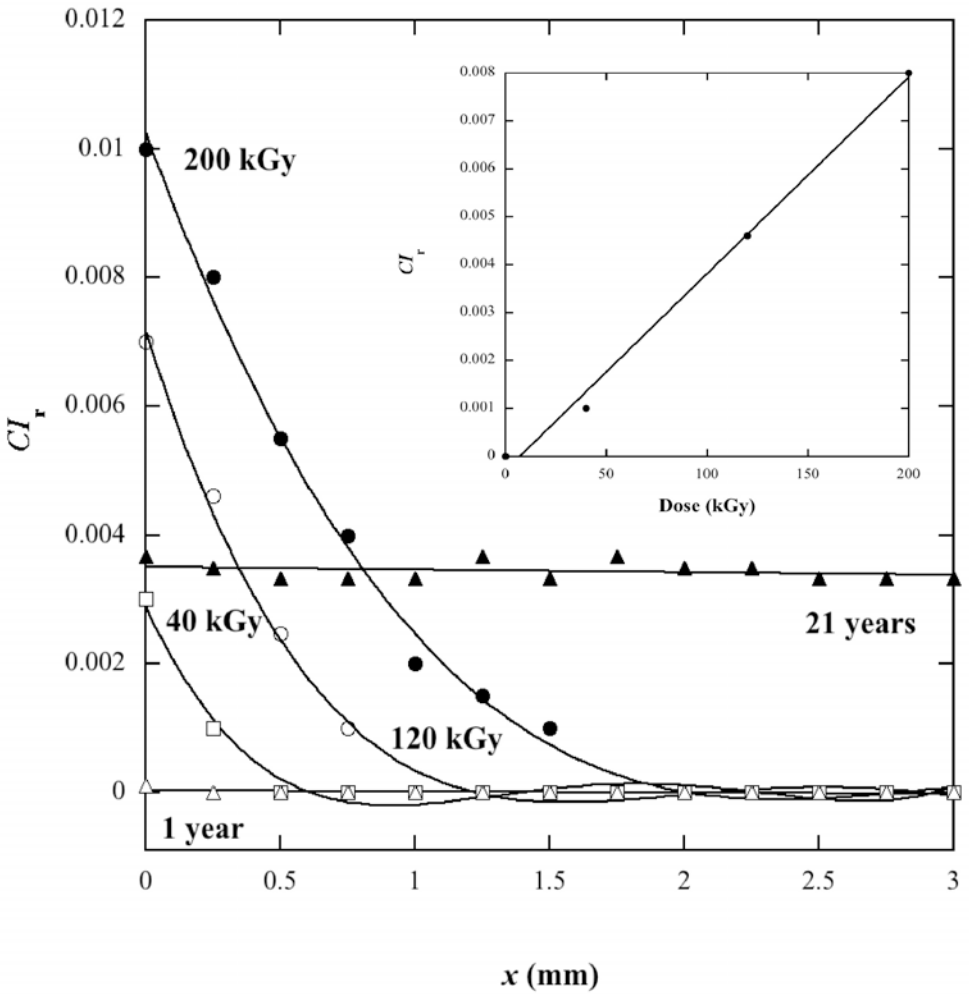
NMR mouse=Non-invasive
No specimen preparation





Radiochemical ageing of highly filled EPDM seals as revealed by accelerated ageing and ageing in-service for 21 years

DLO effects and accelerated ageing
Gamma radiation

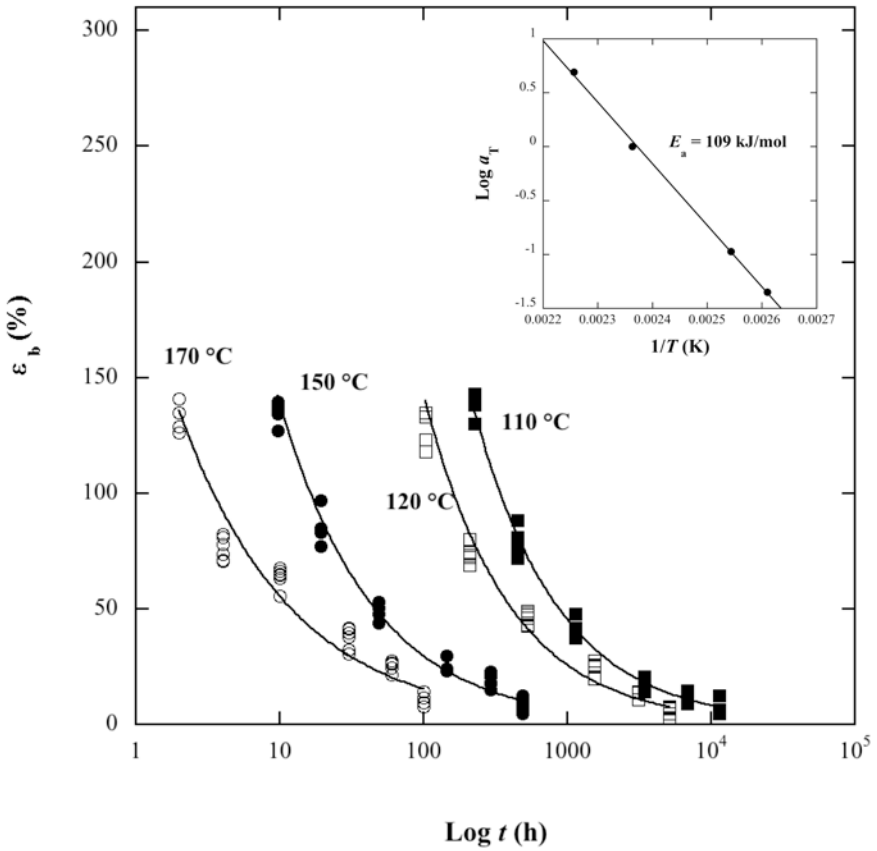


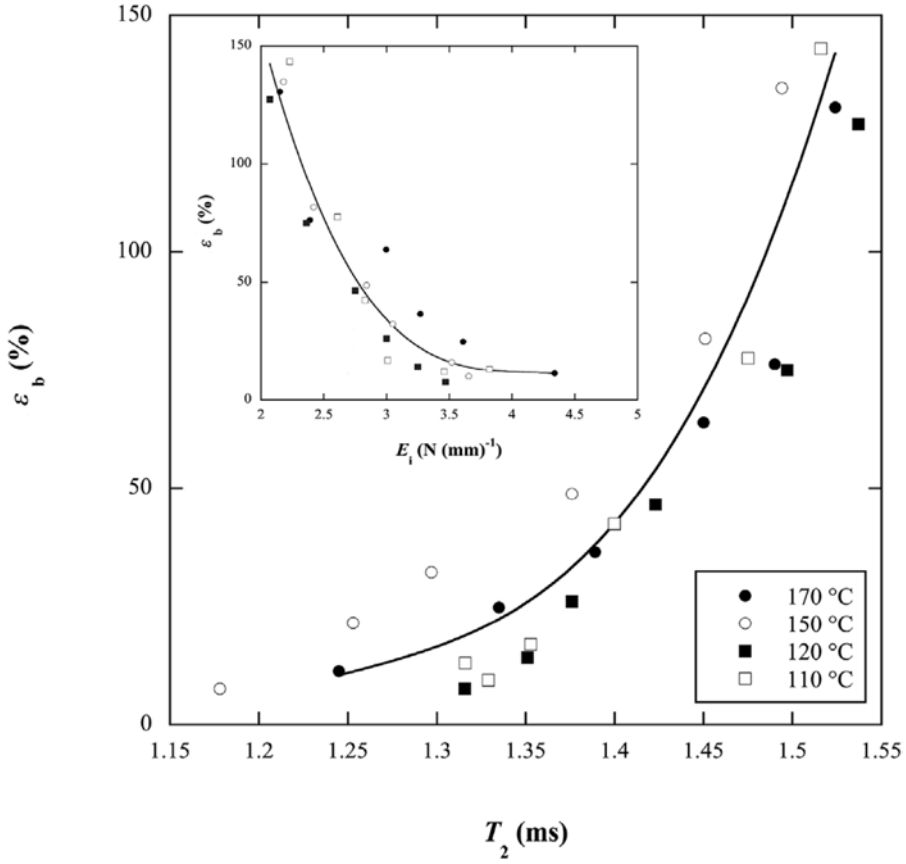
23 C, p_{O2}=1 kPa using ^{60}Co gamma-ray source that yielded a dose rate of 0.31 kGy/h

Service conditions
23 C, p_{O2}=1 kPa
0.15 kGy/year.

P. Pourmand, M. S. Hedenqvist, I. Furó, U. W. Gedde, *Polym. Degr. Stab.* **144** (2017) 473-484.

Deterioration of highly filled EPDM rubber by thermal ageing in air: kinetics and non-destructive monitoring



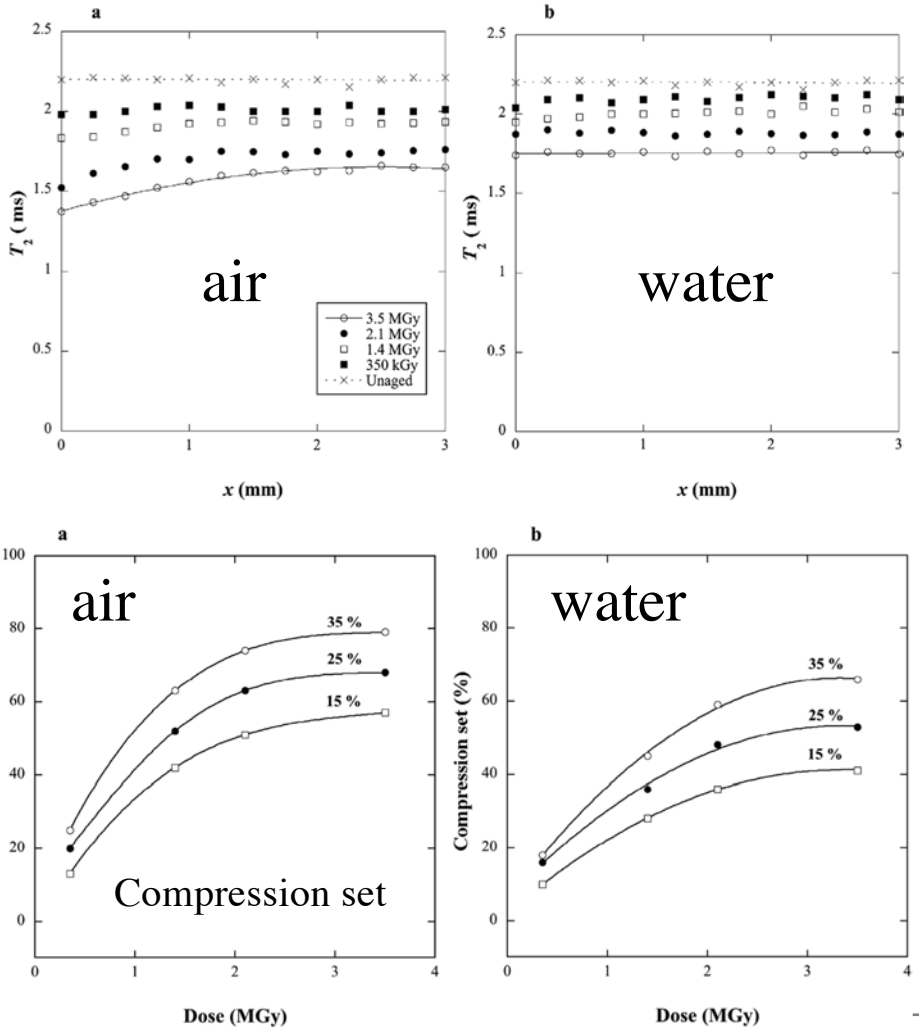


ε_b=50 %, 3000 years at 23 C

P. Pourmand, M.S. Hedenqvist, I. Furó, U.W. Gedde, *Polym. Test.* **64** (2017) 267-276.

Effect of gamma radiation on carbon-black-filled EPDM seals in water and air

oxidative crosslinking
(but also anaerobic crosslinking)



$$H_2O \xrightarrow{\gamma} (H_2O^{\bullet+})^* + e^- \rightarrow e_{aq}^-$$
$$\downarrow 10^{-13}\ s$$
$$H_{aq}^+ + {}^{\bullet}OH_{aq}$$

$$e_{(aq)}^- + O_2 \rightarrow O_2^{\cdot -}$$

$$2O_2^{\cdot -} + 2H^+ \rightarrow H_2O_2 + O_2$$

$$e_{(aq)}^- + H_2O_2 \rightarrow {}^-OH + {}^{\cdot}OH$$

$$O_2^{\cdot -} + H^+ \rightarrow HO_2^{\cdot}$$

$$O_2^{\cdot -} + HO_2^{\cdot} \rightarrow O_2 + HO_2^- = H_2O_2 \quad (pKa = 11.9)$$

oxygen dissolved in water is
consumed during irradiation,
less oxygen available for oxidation

short exposure (40 h) to 350 kGy once per year

P. Pourmand, L. Hedenqvist, A. M. Pourrahimi, I. Furó, T. Reitberger, U.W. Gedde, M.S. Hedenqvist, *Polym. Degr. Stab.* **146** (2017) 184-191.

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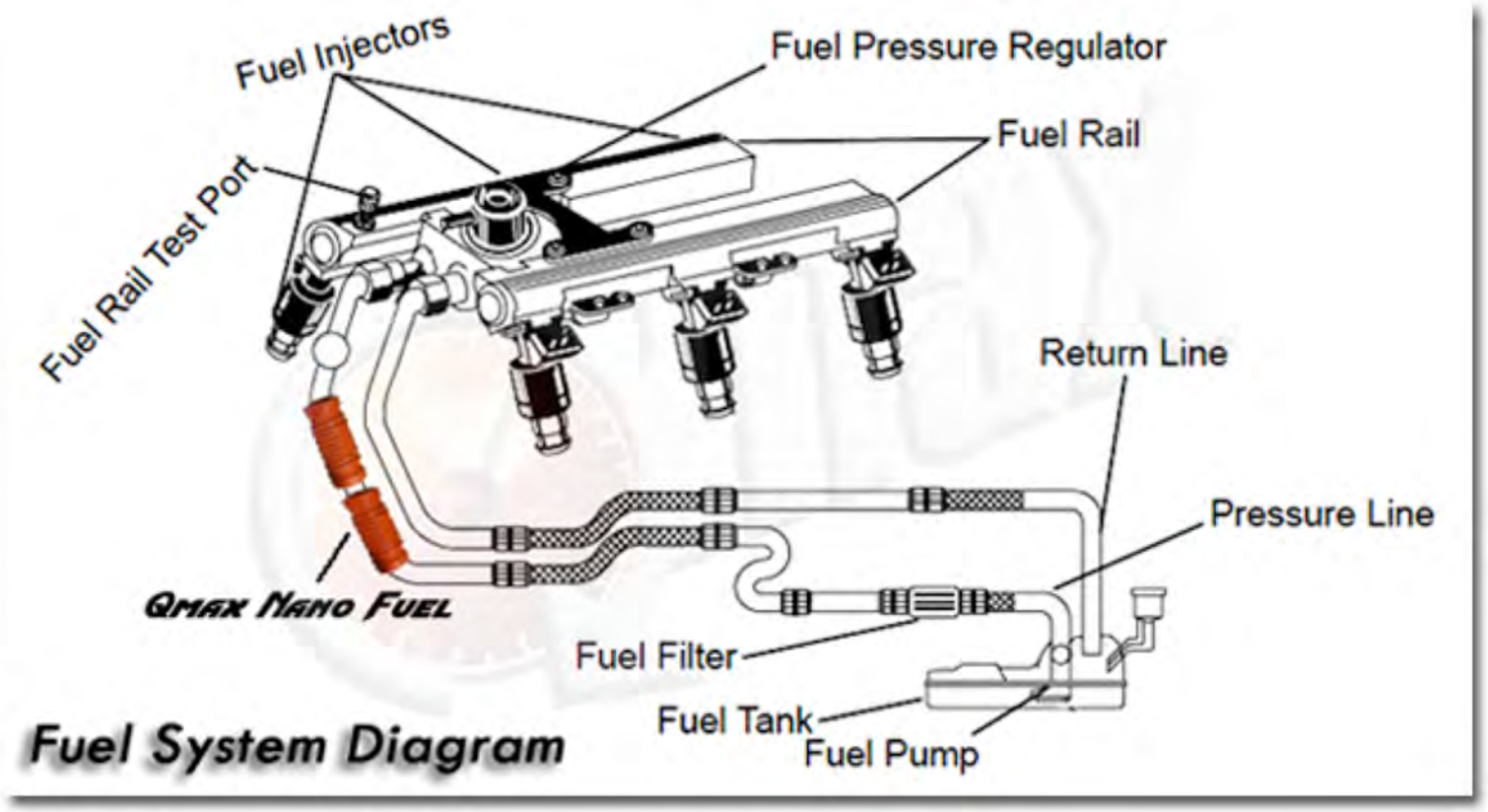
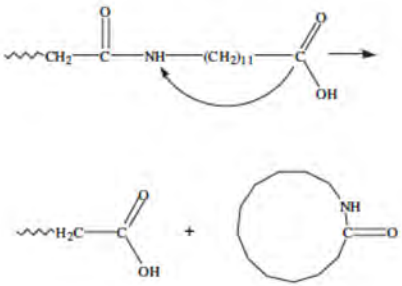
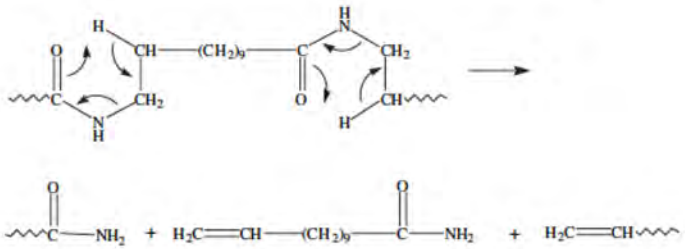
Automotives



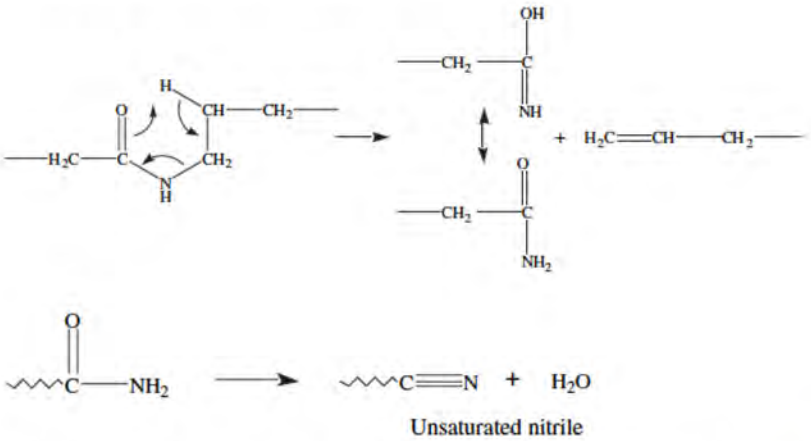
1.1 Intramolecular exchange



1.2 Cis-elimination with alkylamide bond splitting



1.3 Cis-elimation and dehydration

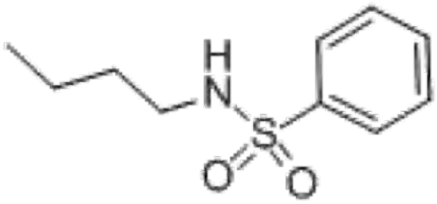


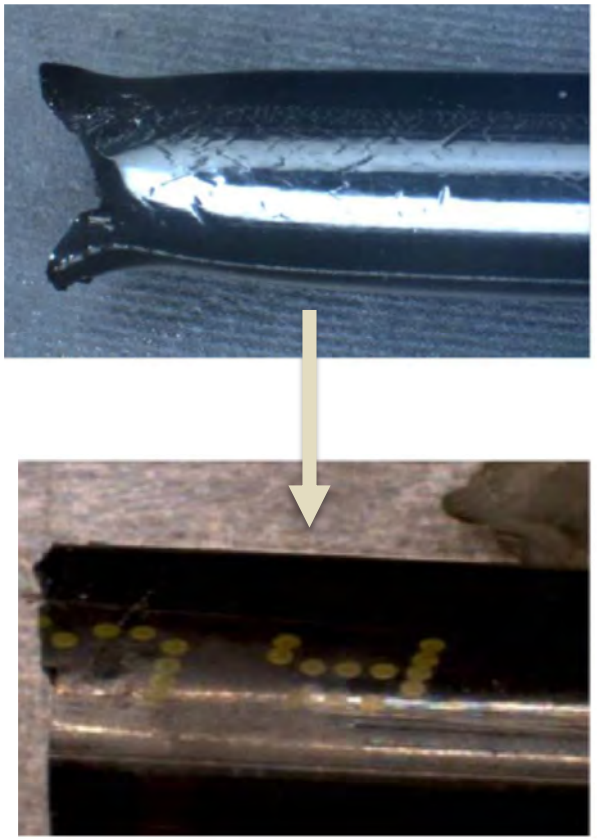
Scheme 1. The three mechanisms of thermal degradation in inert and oxidative environments of PA12 [9–12].

Polyamide-12

Petrol/ethanol

Molar mass reduction
Plasticiser loss





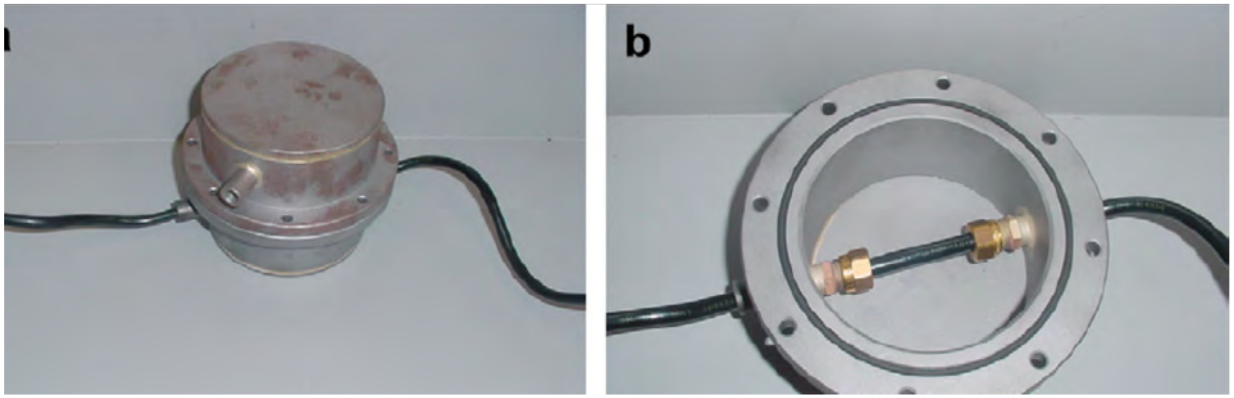
Molar mass data of inner surface regions of pipes aged at 110 °C

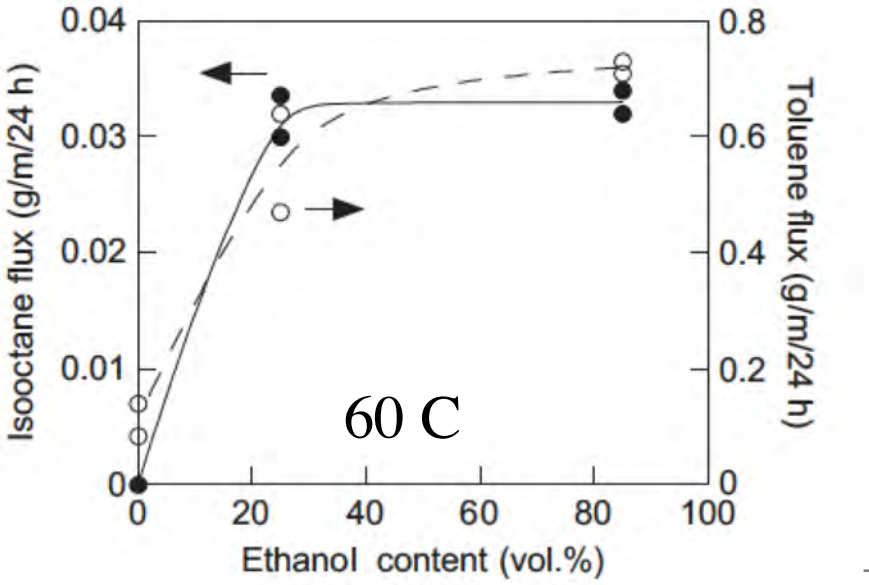
Fuel	Ageing time (h)	$\overline{M}_w$ (kg/mol)	$\overline{M}_w/\overline{M}_n$
Unaged	0	144	2
E0	1200	65	1.8
E0	1800	72	3.3
E0	2400	62	2.5
E10	1200	39	3.5
E10	2400	72	2.2
E30	1200	76	2
E30	1800	61	2.1
E30	2400	45	2.9

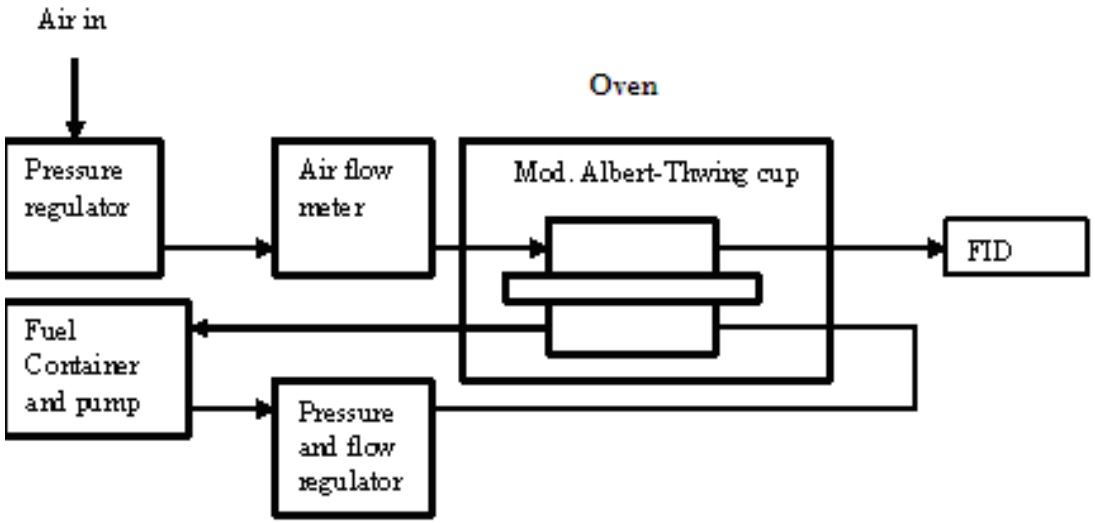
K. Kallio and M. S. Hedenqvist, *Polym. Degr. Stab.* **93** (2008) 1846-1854.

Fuel permeation through pipes

Fuel C
50 vol% Isooctane
50 vol% Toluene

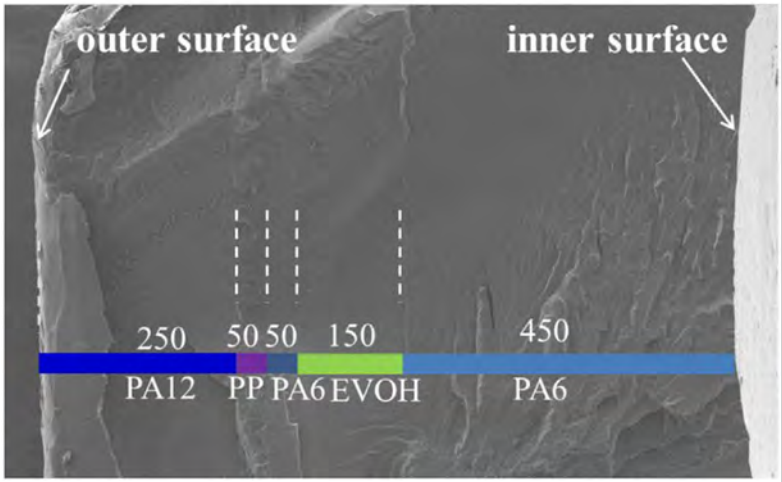


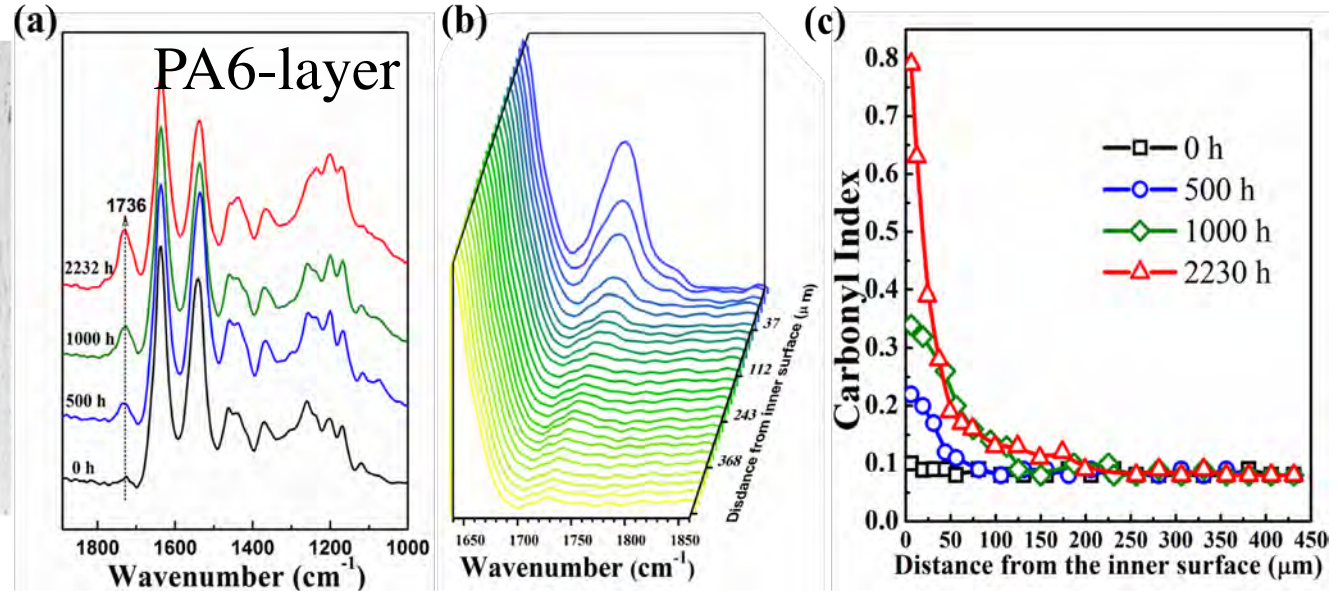


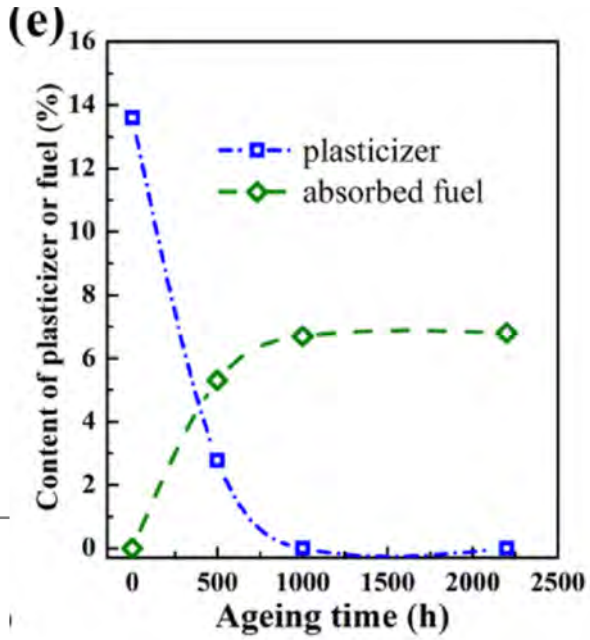


K. Kallio, M. S. Hedenqvist *Polym. Test.* **29** (2010) 603-608.

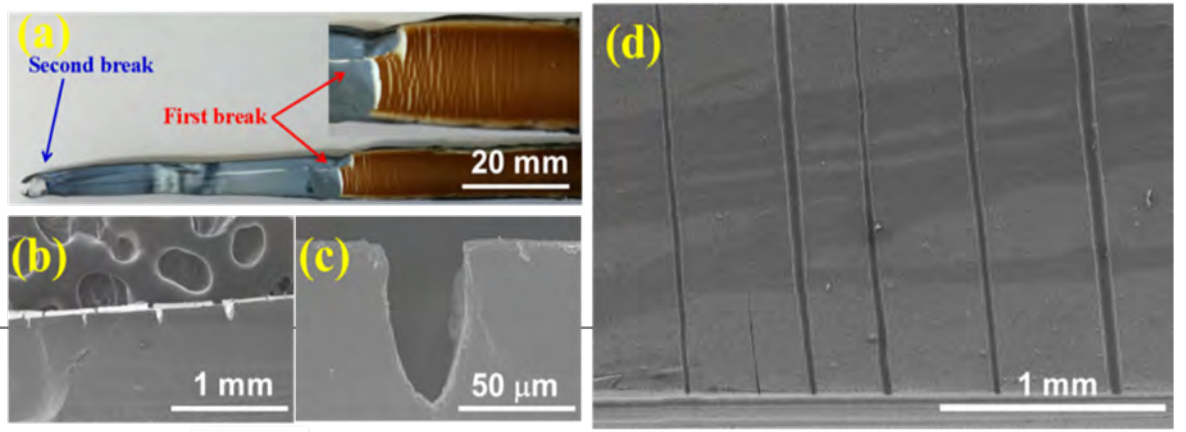
Long-term performance of polyamide-based multilayer (bio)diesel fuel lines aged under "in-vehicle" conditions







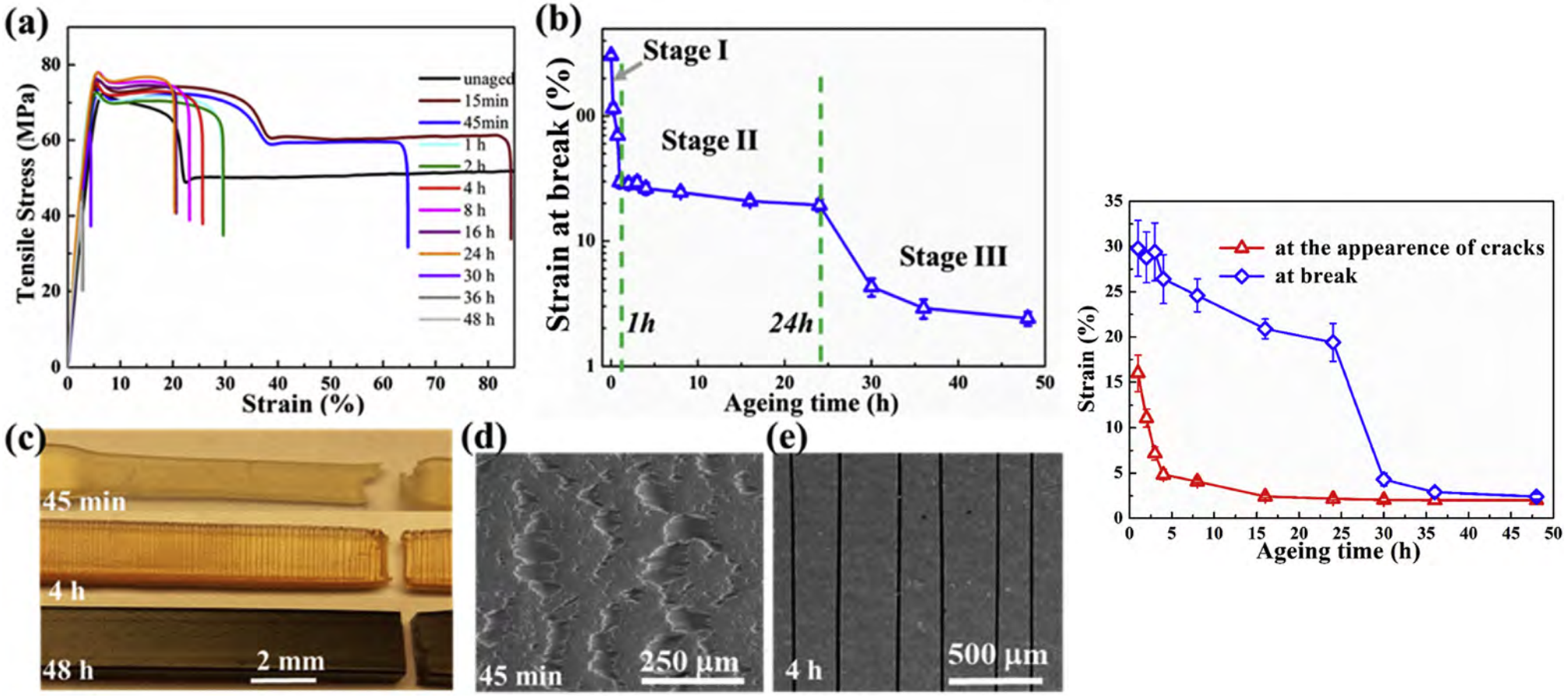
Alternatively petroleum-diesel (B0) and B0 with 20 % biodiesel (B20)



X. Wei, S. Akhlaghi, K. J. Kallio, S. Bruder, M. Bellander, U. W. Gedde, M. S. Hedenqvist, *Polym. Degr. Stab.*, **144** (2017) 100-109.

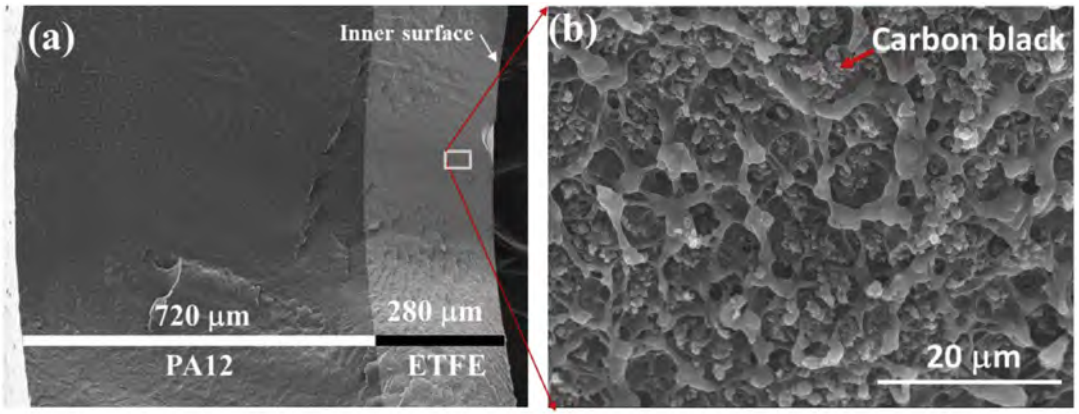
PA6
180 C
Dry air

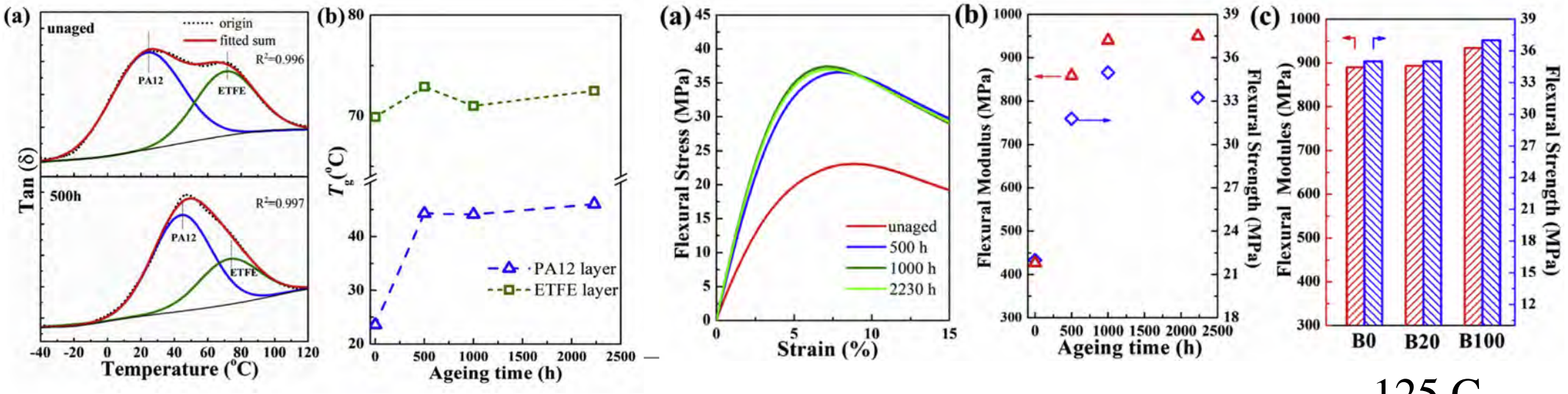
Diffusion-limited Oxidation of Polyamide: Three Stages of Fracture Behavior



X.-F. Wei[a], K. J. Kallio, S. Bruder, M. Bellander, H.-H. Kausch, U. W. Gedde, M. S. Hedenqvist, *Polym. Degr. Stab.*, **154** (2018) 73-83.

Long-term performance of a polyamide-12-based fuel line with a thin ETFE inner layer exposed to bio- and petroleum diesel



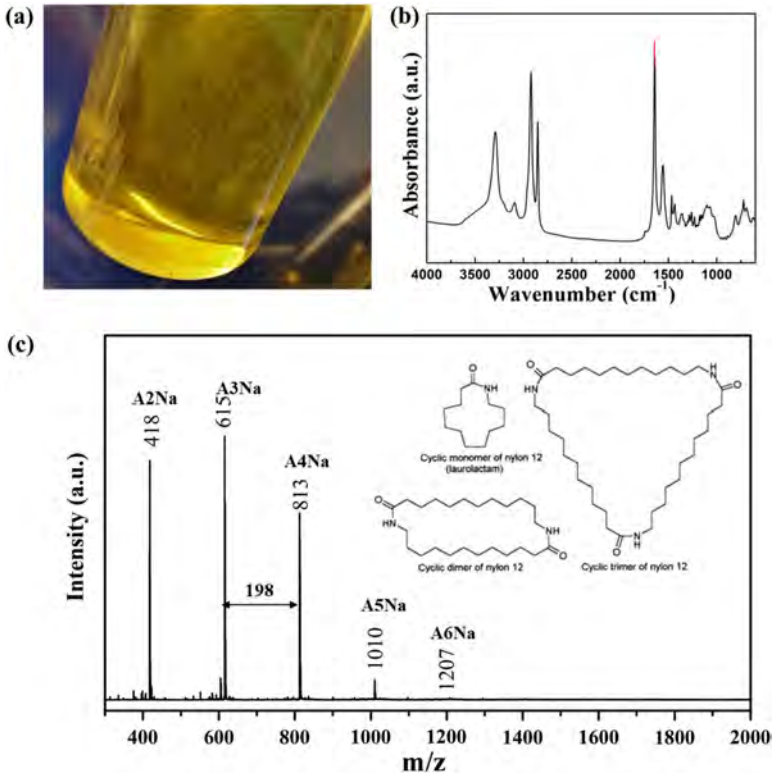


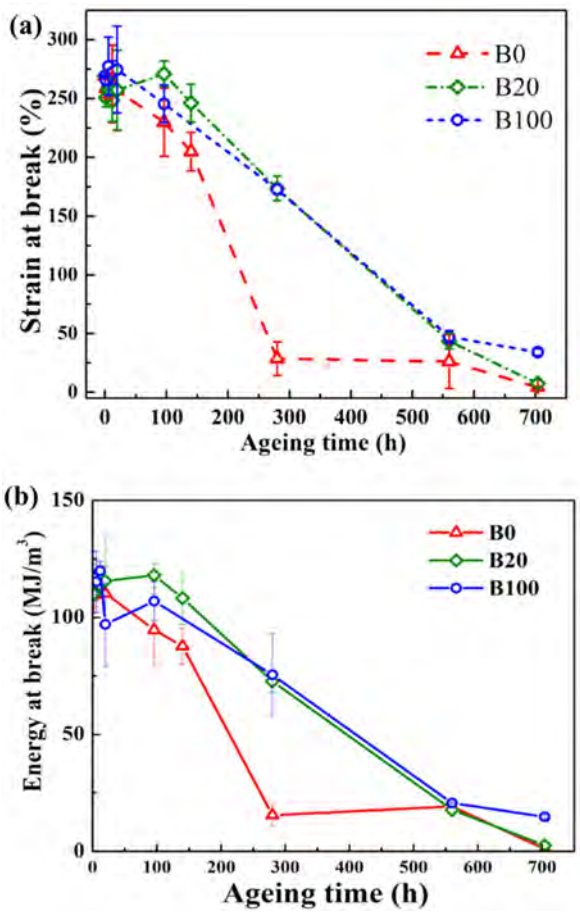
125 C

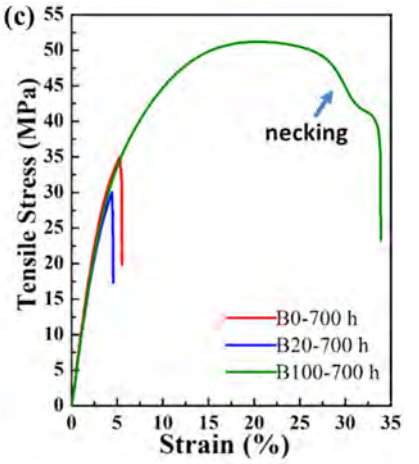
X.-F. Wei, K. J. Kallio, S. Bruder, M. Bellander, U. W. Gedde, M. S. Hedenqvist, *Polym. Degr. Stab.*, **156** (2018) 170-179.

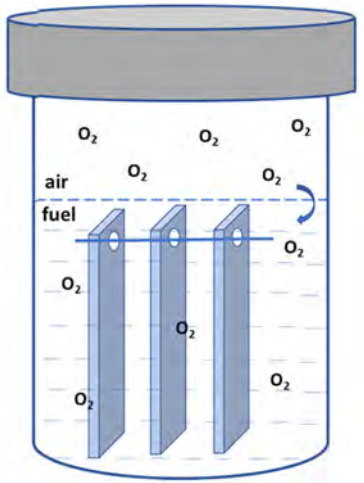
Polyamide 12 exposed to (bio)diesel at high temperature: Ageing properties and polymer/fuel interactions

125 C



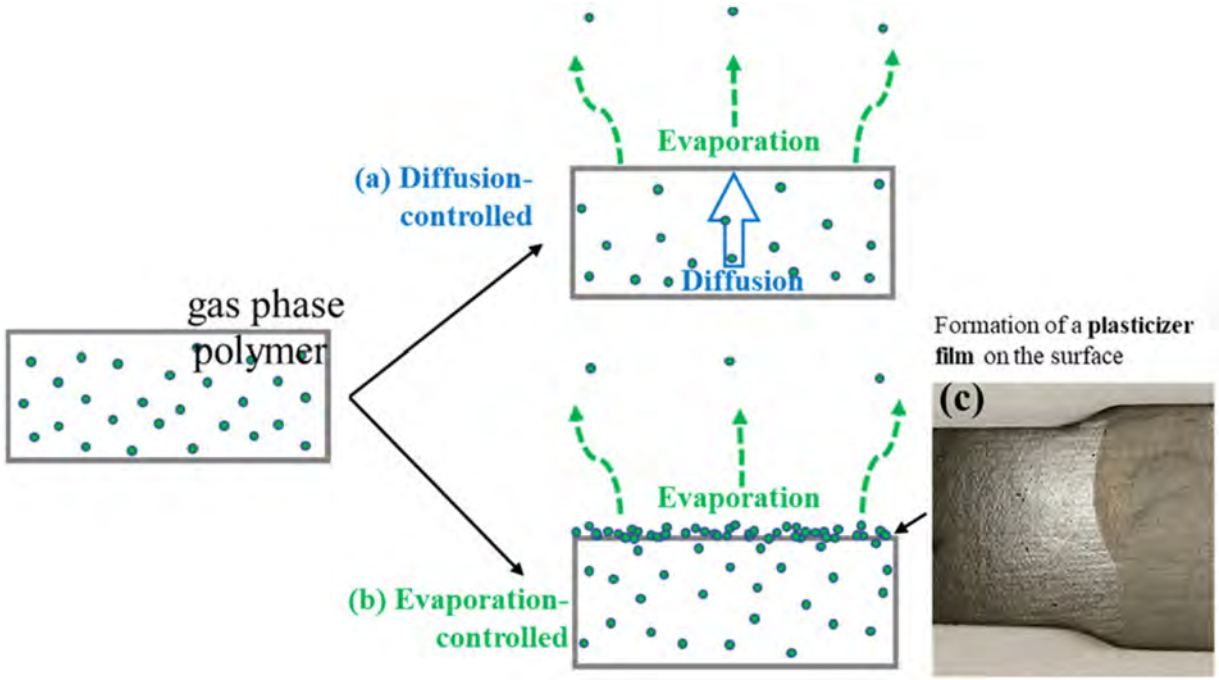


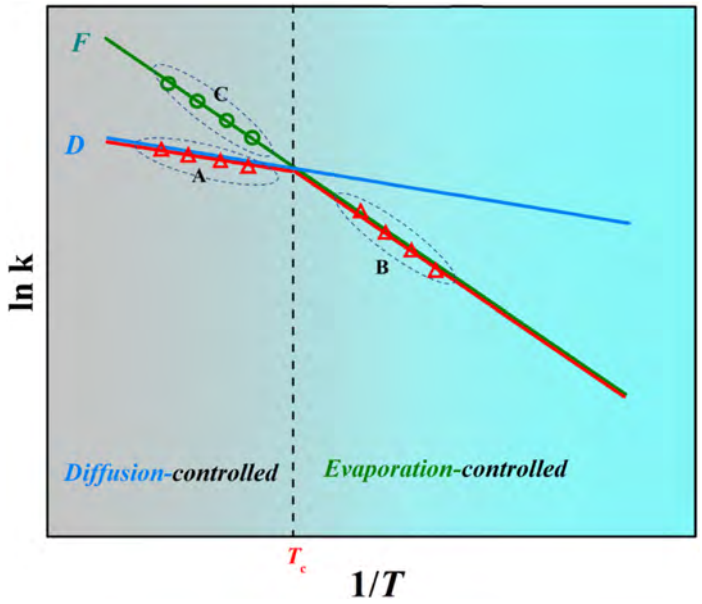


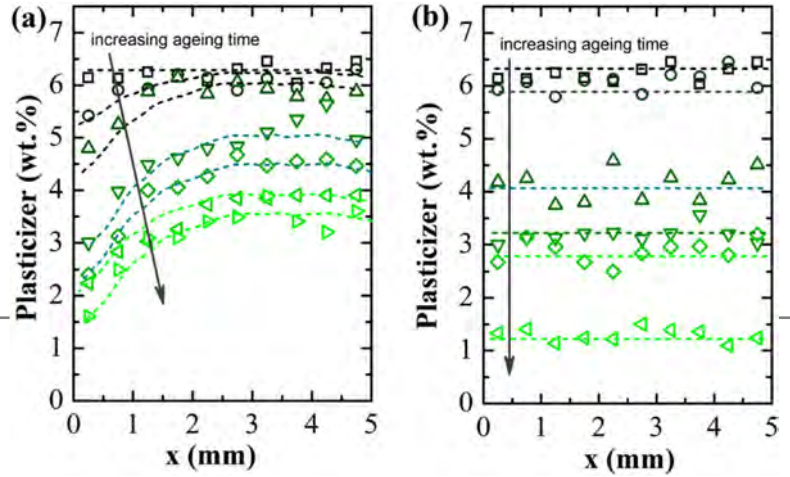


X.-F. Wei, L. De Vico , P. Larroche, K. J. Kallio, S. Bruder, M. Bellander, U. W. Gedde, M. S. Hedenqvist, *npj Mater. Degrad.*, **3** (2019) 1-11.

Plasticiser loss from plastic or rubber products through diffusion and evaporation







Prediction over Tg
Complex, safety factor
Case: PA12 125 C to 60 C

X.-F. Wei, E. Linde, M. S. Hedenqvist, *npj Mater. Degrad.*, **18** (2019) 1-8.

Rubbers in fuel/engine parts of vehicles

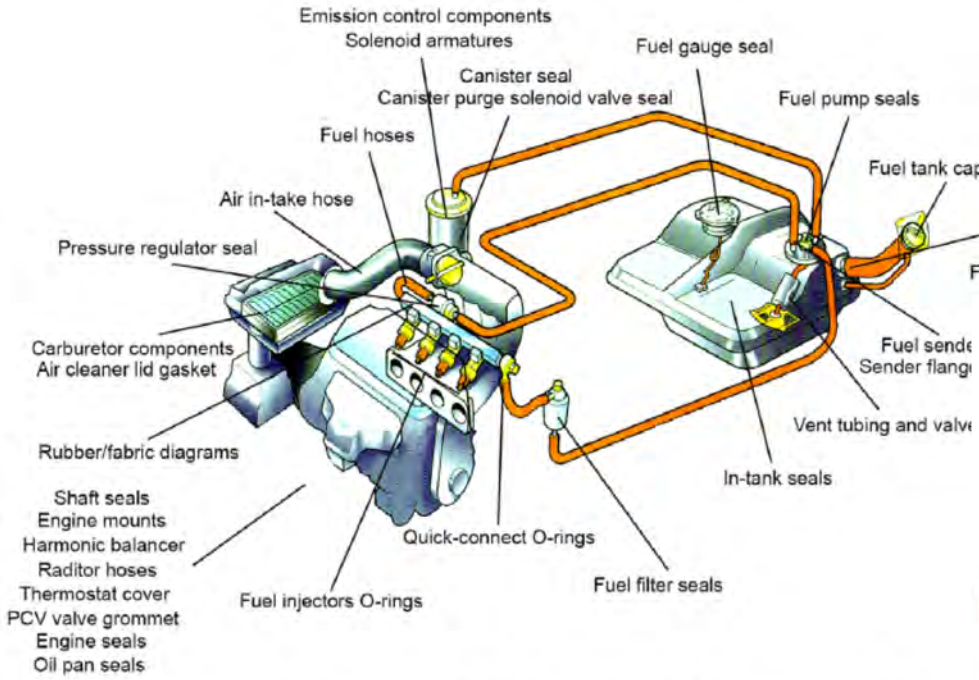


Fig. 1. The location of some of the rubber parts in a conventional fuel syster

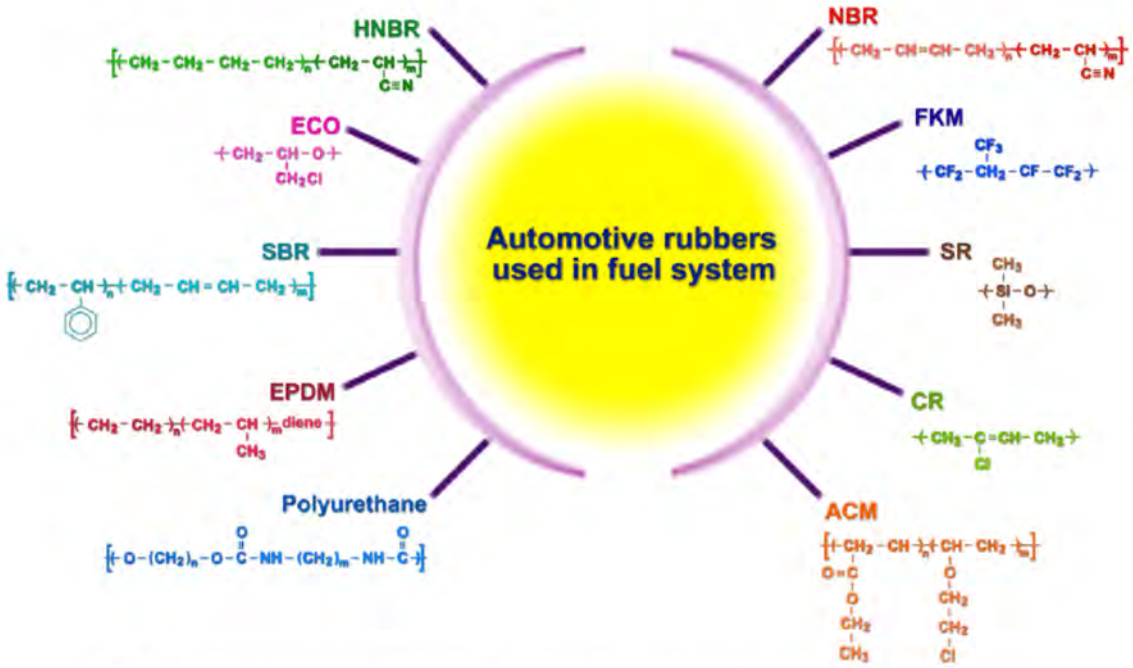


Fig. 2. Chemical structures of the rubbers most frequently used in automobile fuel systems.

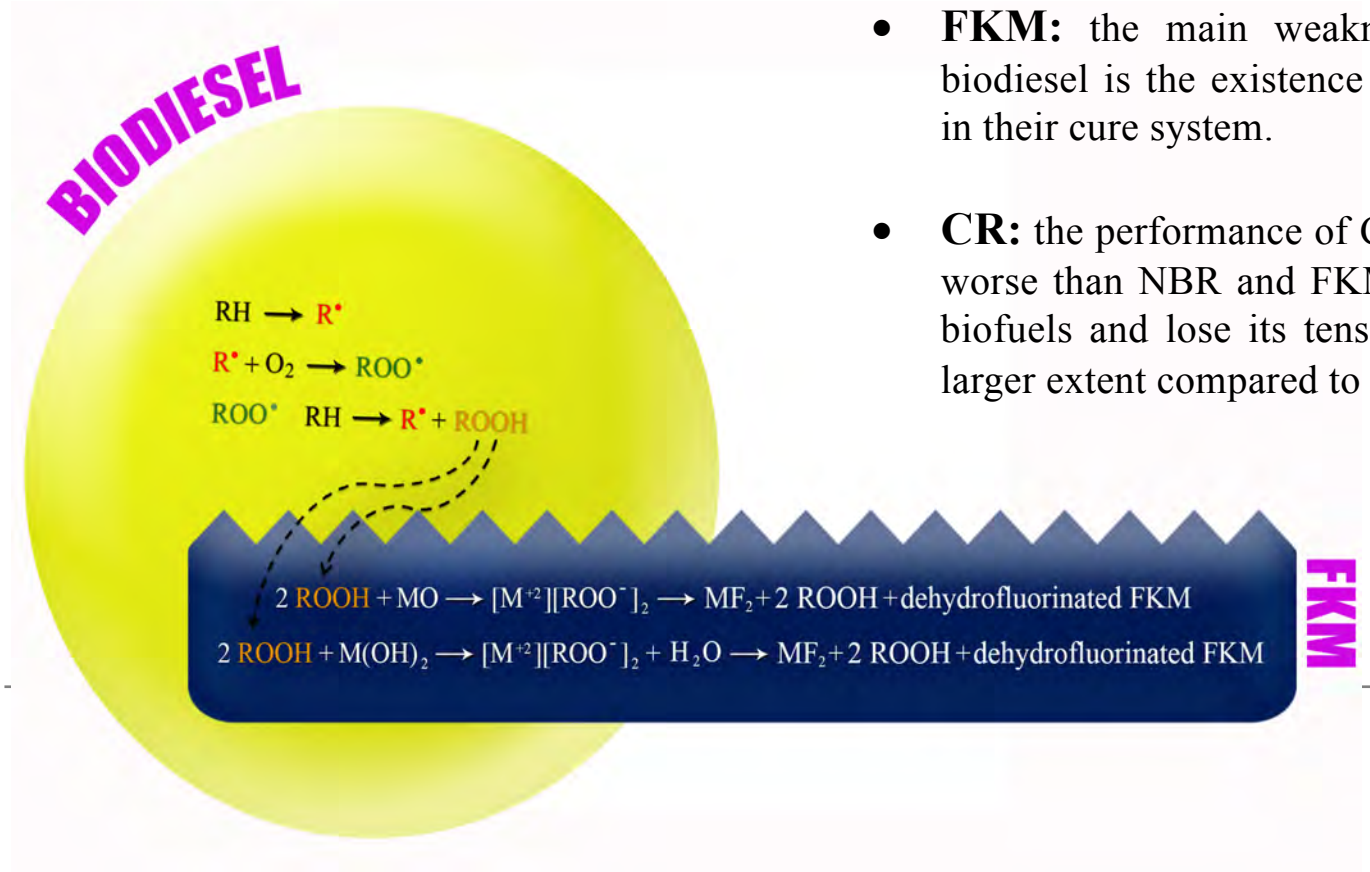
"Deterioration of **Automotive Rubbers in Biofuels**: A Review", S. Akhlaghi, M. S. Hedenqvist, M. T. Conde Braña, M. Bellander and U. W. Gedde, *Renew. Sustain. Energy Rev.* **43** (2015) 1238-1248.

Rubbers in fuel/engine parts of vehicles

- **NBR:** the physical and mechanical properties of NBR decrease after exposure to almost all the commercially available biofuels. NBR resistance to biofuels is improved by increasing ACN% of the rubber compound as well as using sulfur cure system instead of peroxide-based crosslinking system.

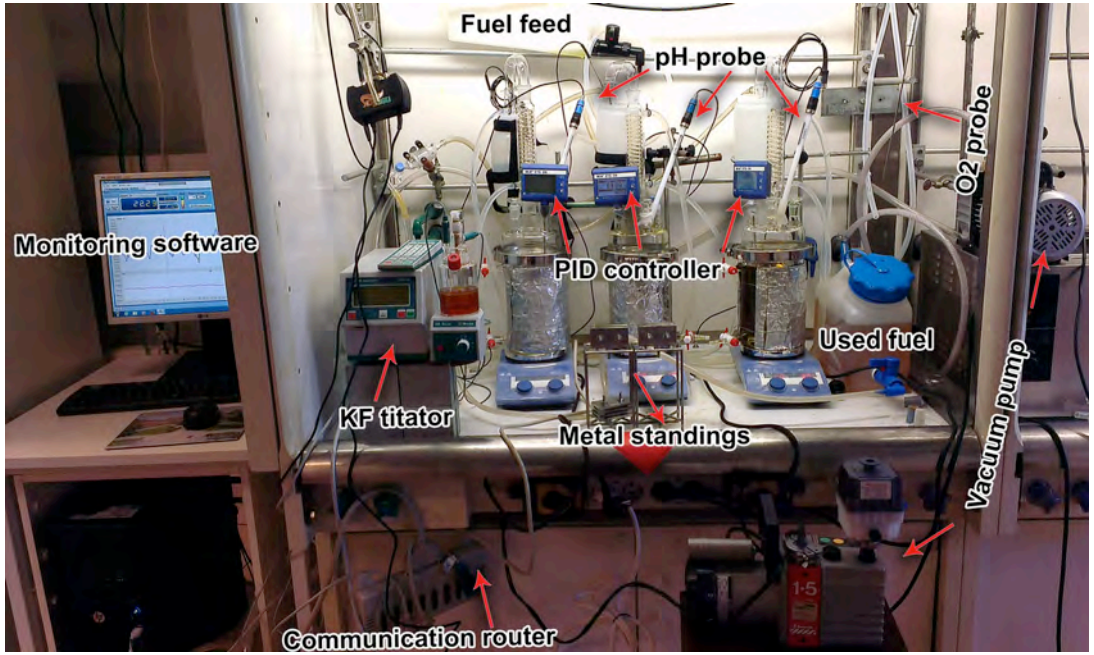
- **FKM:** the main weakness of FKM rubbers towards biodiesel is the existence of metal oxides and hydroxides in their cure system.

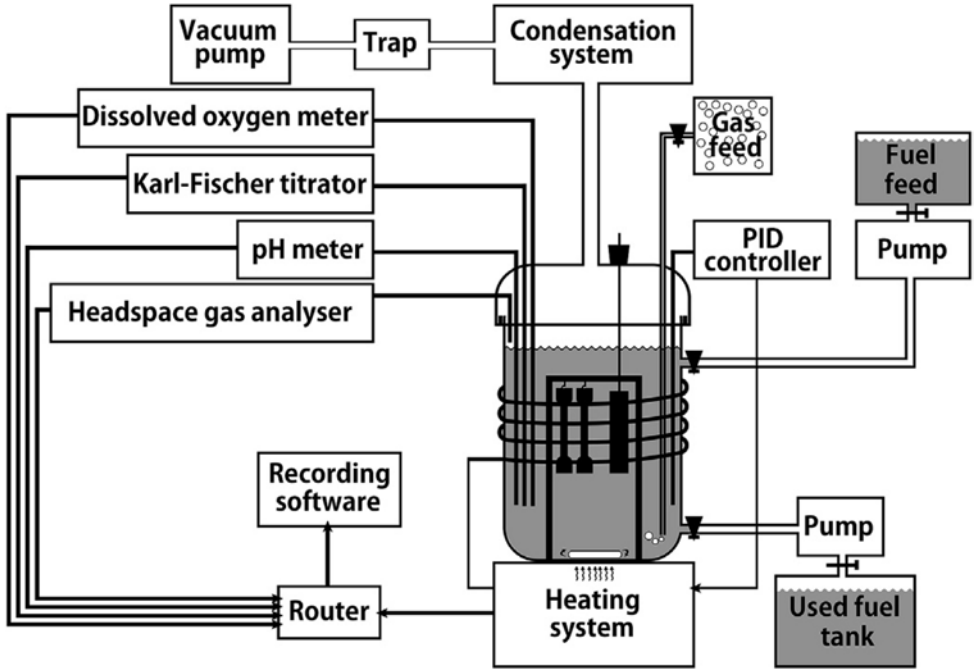
- **CR:** the performance of CR in biodiesel and bioethanol is worse than NBR and FKM. CR swells much more in the biofuels and lose its tensile properties and hardness to a larger extent compared to FKM and NBR.



Plastic/rubber immersed in fuel

fuel: water/O2 content, acidity





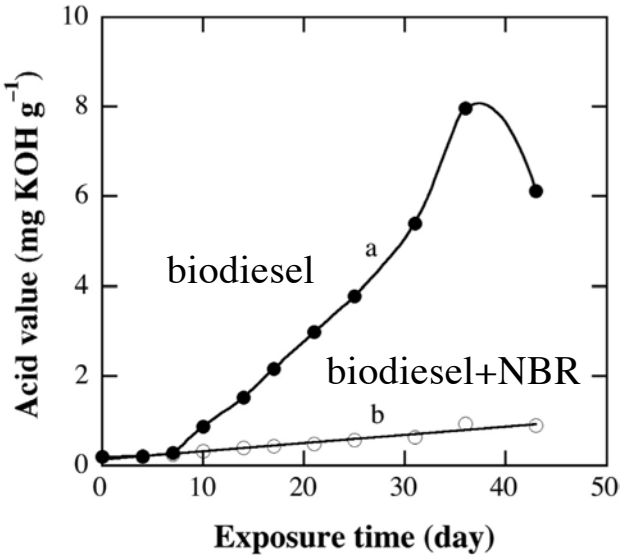
Nitrogen/oxygen gas purge into the fuel

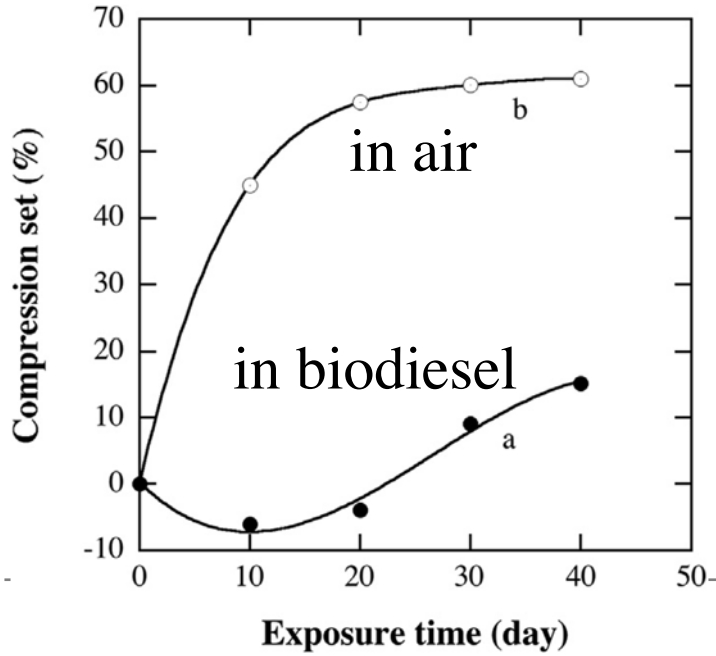
Creating different $p_{O2,}$ removal of headspace if necessary

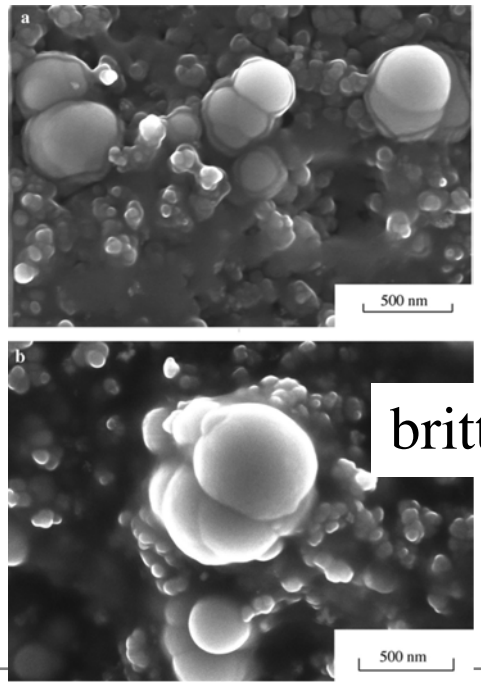
Deterioration of **NBR rubber in rapeseed biodiesel**

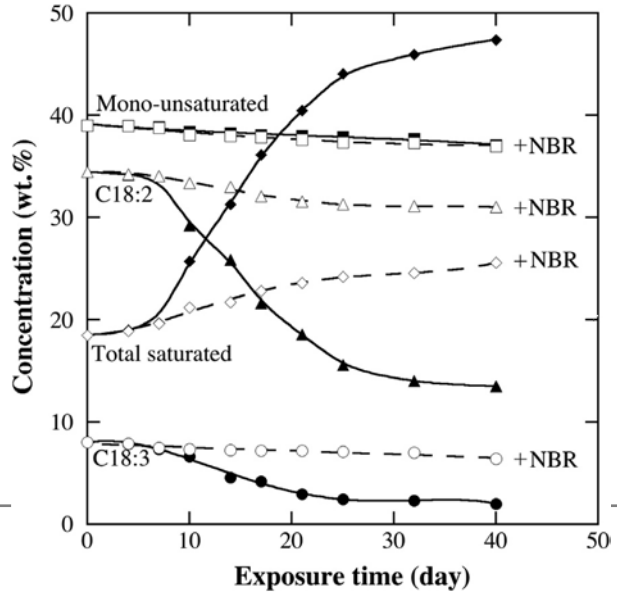
-migration of stabilizer/plasticiser from the rubber to biodiesel
-diffusion of dissolved oxygen from biodiesel into NBR
-absorption of oxidation precursors of biodiesel by the rubber
-internal cavitation was caused by the attack of biodiesel on the acrylonitrile units of NBR
-biodiesel-induced swelling of rubber

90 C



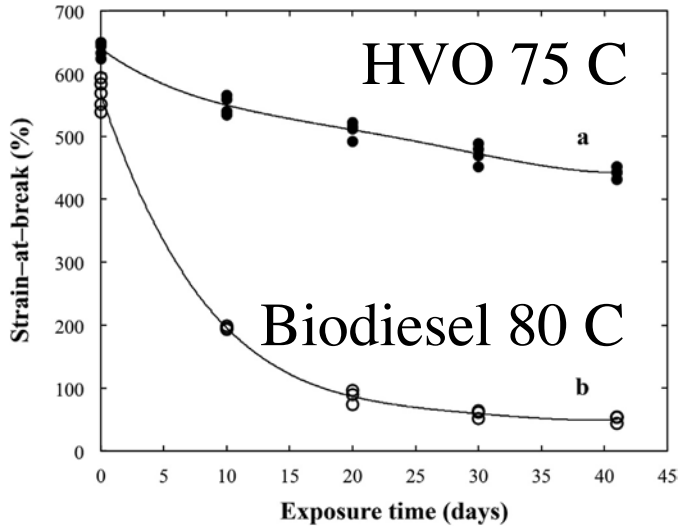






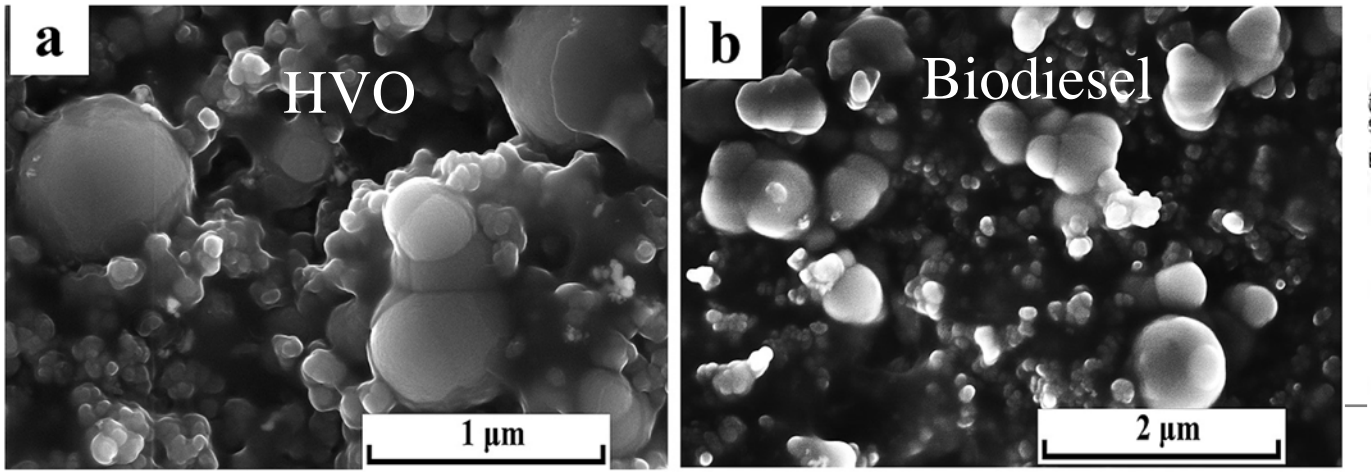
S. Akhlaghi, M. S. Hedenqvist, M. T. Conde Braña, M. Bellander, U. W. Gedde, *Polym. Degr. Stab.* **111** (2015) 211-222.

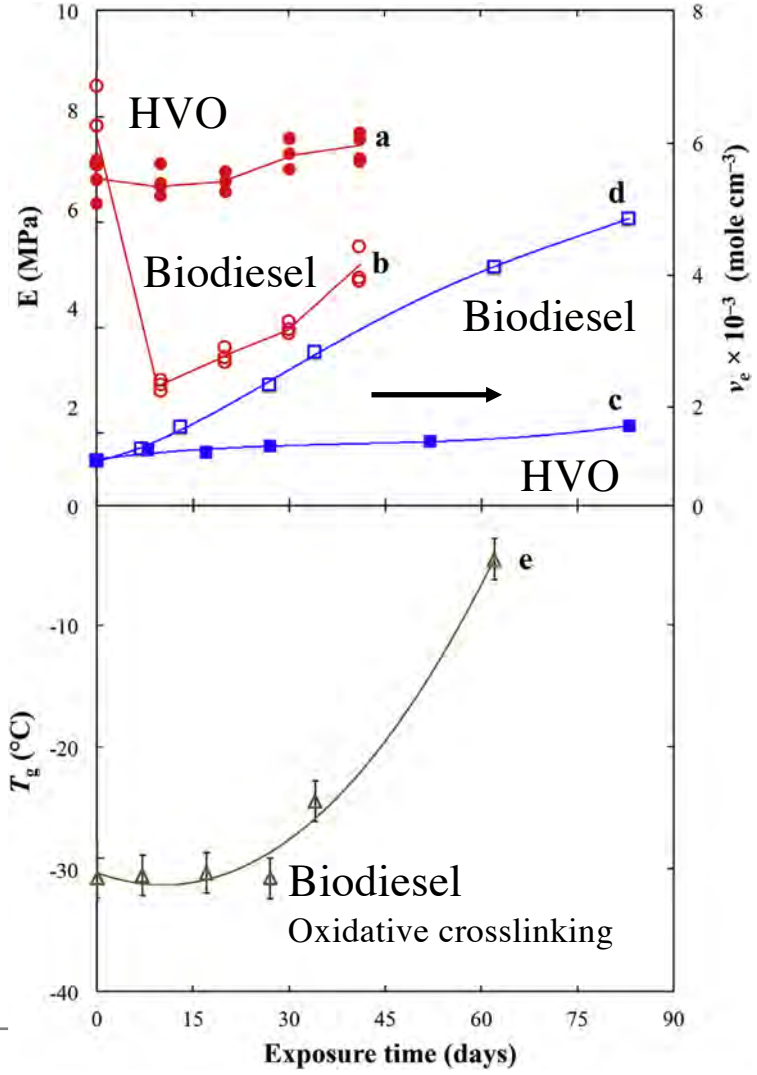
Degradation of carbon black–filled–**NBR** **in biodiesel and HVO**



Loss of plasticiser

Cavitation in the filler-rubber interphase (biodiesel)





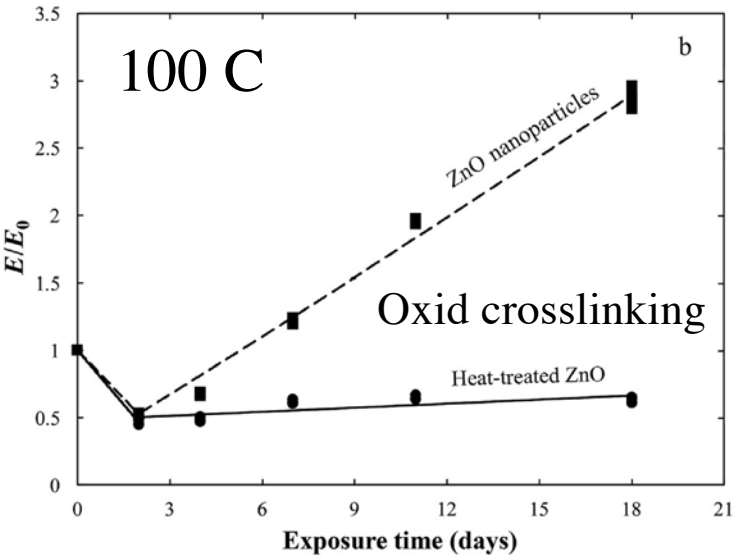
S. Akhlaghi, A.M. Pourrahimi, M. S. Hedenqvist, C. Sjöstedt, M. Bellander, U. W. Gedde, *Polym. Degrad. Stab.* **123** (2016) 69-79.

Effects of ageing conditions on **degradation of NBR rubber filled with heat-treated ZnO** star-shaped particles in rapeseed biodiesel

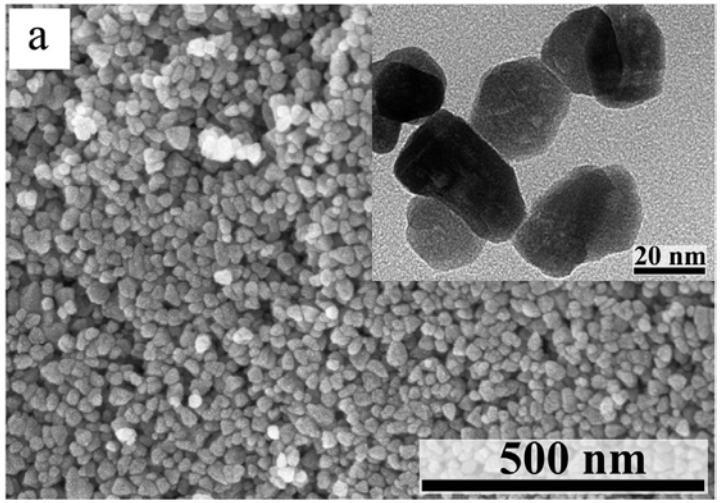
Effects of biodiesel (80 C, acidic)

$$ZnO_{(s)} + 2H^{+}_{(aq)} \leftrightharpoons Zn^{2+}_{(aq)} + H_2O_{(l)}$$

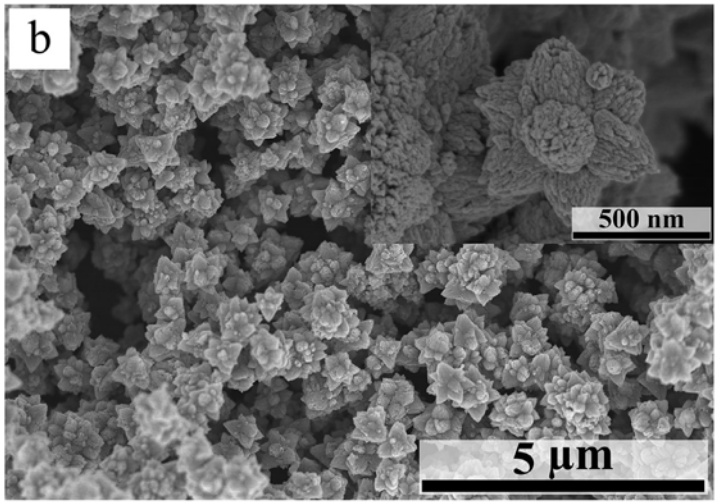
Zn^{2+} attacks the nitrile group,
less hydrophilic and takes up more fuel



Nanoparticles

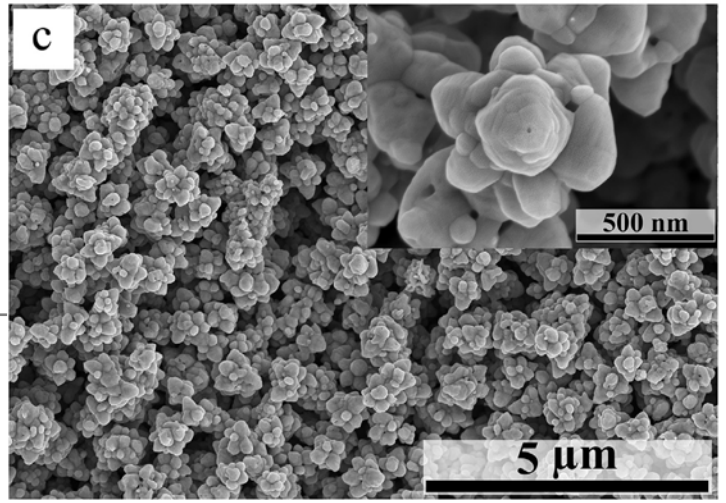


Star-shaped
Better dispersed



Heat-treated

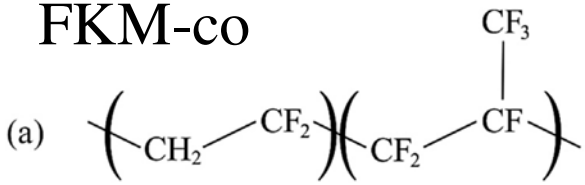
Porous-free less reactive



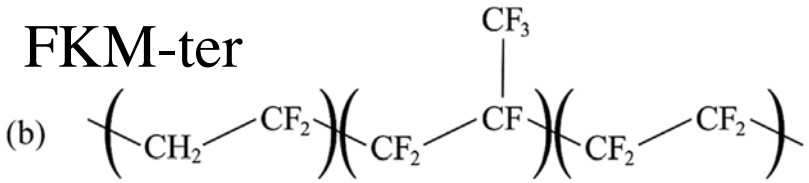
S. Akhlaghi, A. M. Pourrahimi, C. Sjöstedt, M. Bellander, M. S. Hedenqvist, U. W. Gedde, *Polym. Degrad. Stab.*, **138** (2017) 27-39.

Degradation of **fluoroelastomers in rapeseed biodiesel**

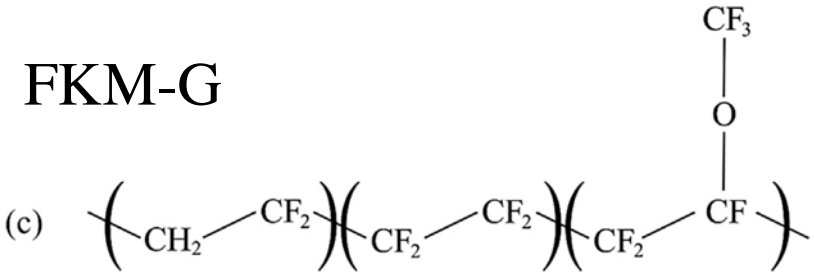
FKM-co



FKM-ter



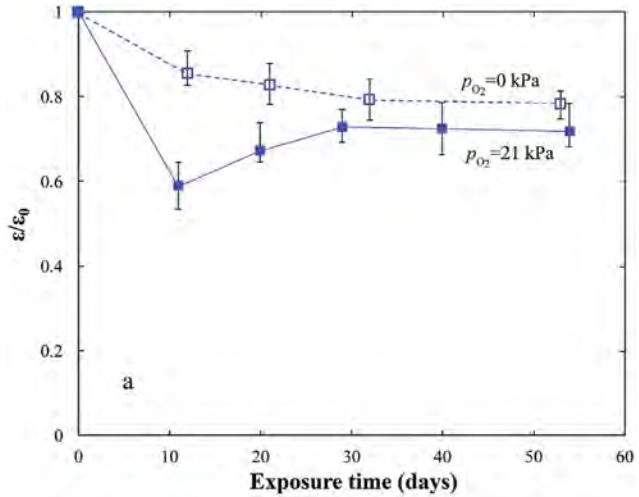
FKM-G

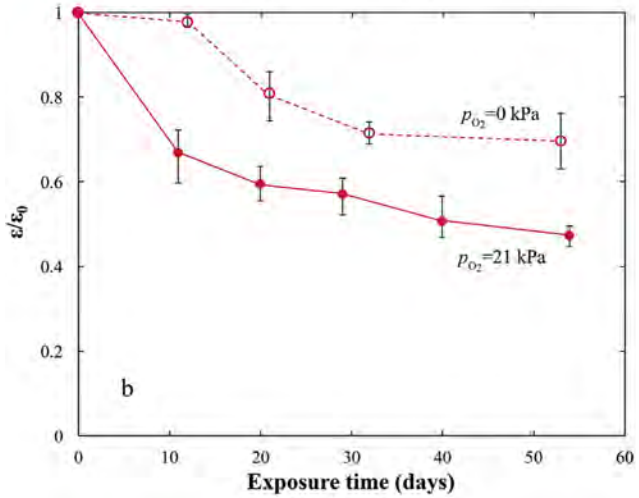


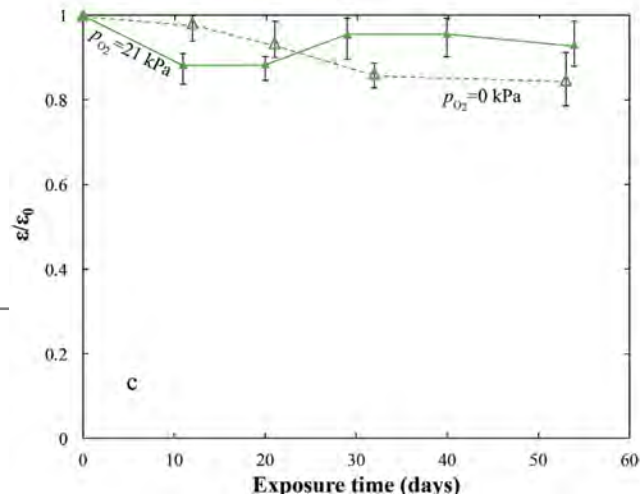
”Dehydroflourination causing chain cleavage”

extensive dehydrofluorination driven by metal ions and rupture of the bound rubber-carbon black network

least amount of unsaturations (where biodiesel attack) and metal oxide/hydroxide particles







S. Akhlaghi, A. M. Pourrahimi, C. Sjöstedt, M. Bellander, M. S. Hedenqvist, U. W. Gedde, *Polym. Degr. Stab.* **136** (2017) 10-19.

Protein plastics/elastomers

Gluten polymers

A stiff ”coin” (no plasticizer)

”Polystyrene / epoxy”

Soft/flexible film (with plasticizer)

”Soft PVC/LDPE”

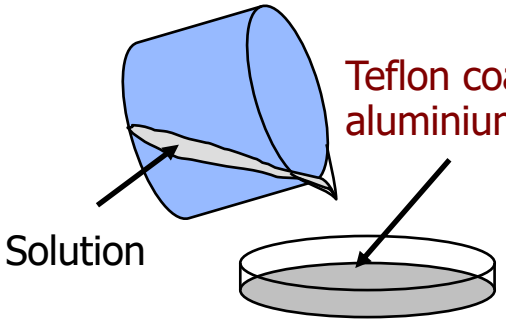
Rubber (more plasticizer)
(Meriplast®, by Tereos-Syral)

Semi-rigid (with plasticizer)

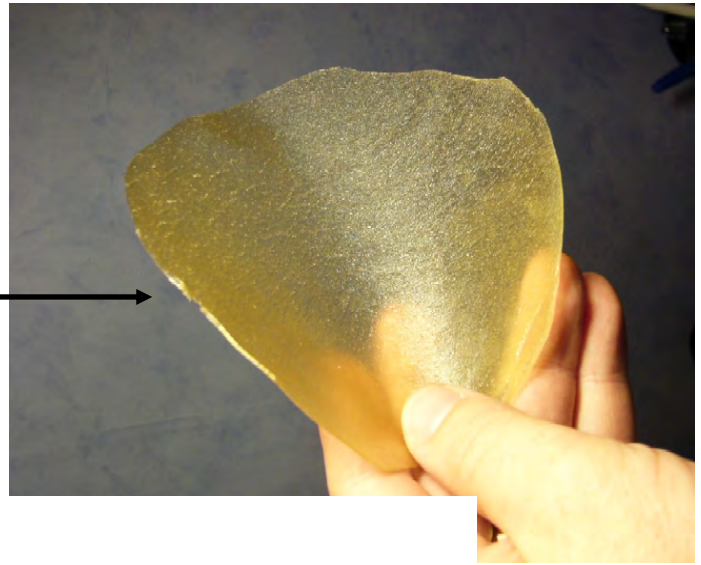
”PP or toughened PS”

Casting

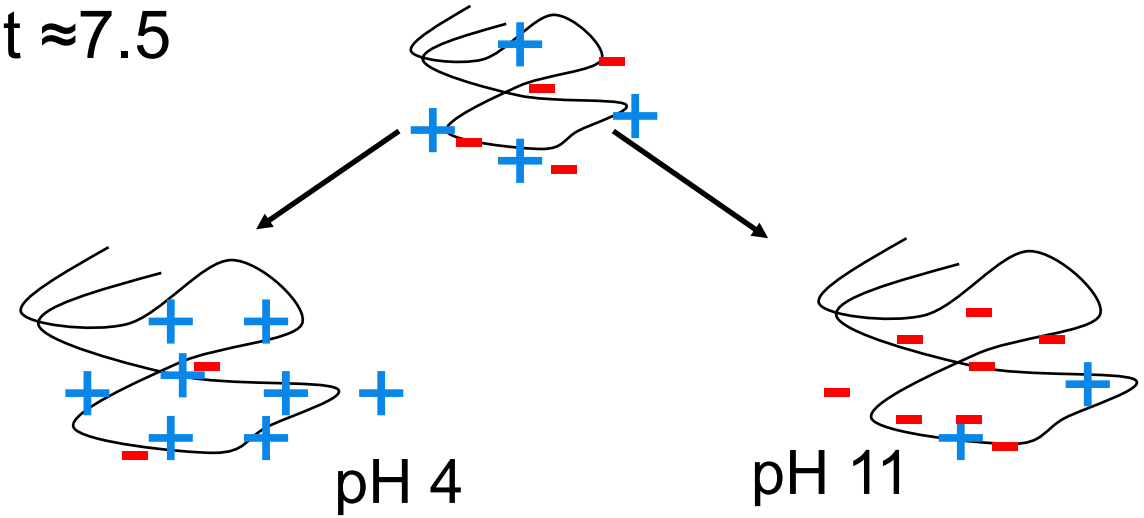
- Gluten
- Glycerol (25 wt%)
- Ethanol
- Water
- pH adjustment
- Heating *up to 75° C (2.5° C/min)*



Drying time: 48 h
Conditions: 50%RH, 23° C



Isoelectric point ≈7.5



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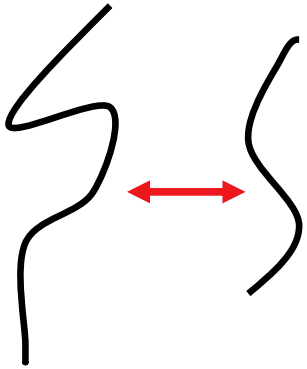
Ext. 1

SDS

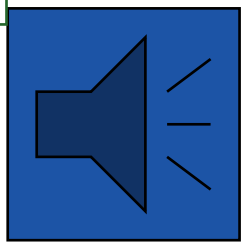
$HO_3SO-(CH_2)_{11}-CH_3$

• Na

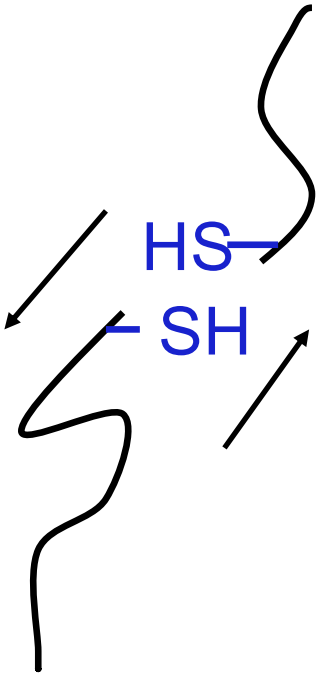


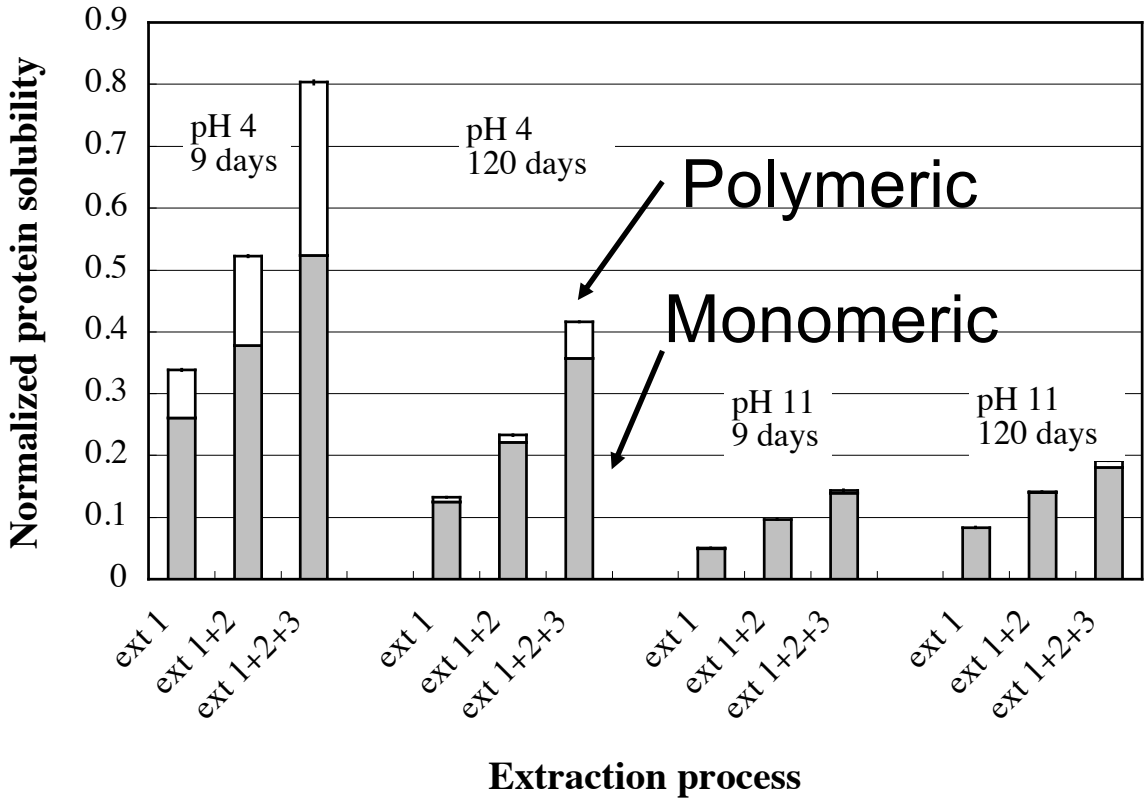
secondary bonds

Ext. 2/3



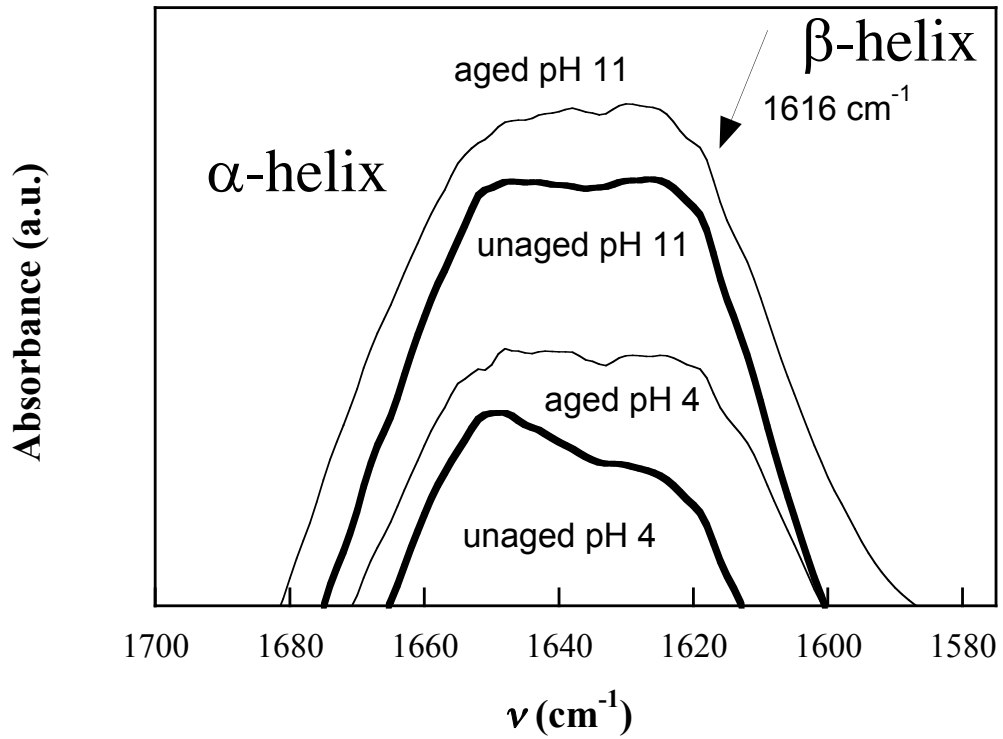
sonication



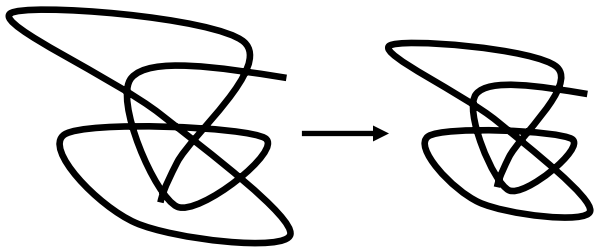


I. Olabarrieta et al., *Biomacromolecules* **7** (2006) 1657-1664.

The amide I region

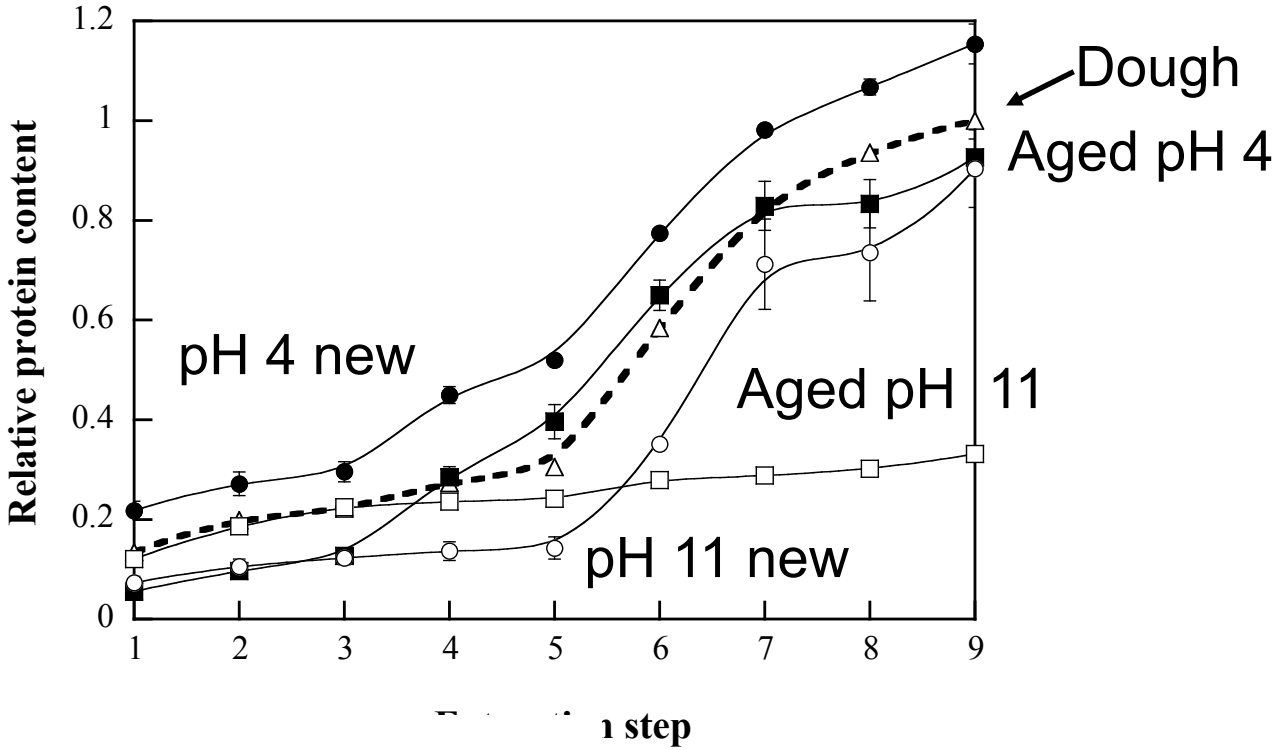


Aggregated structure



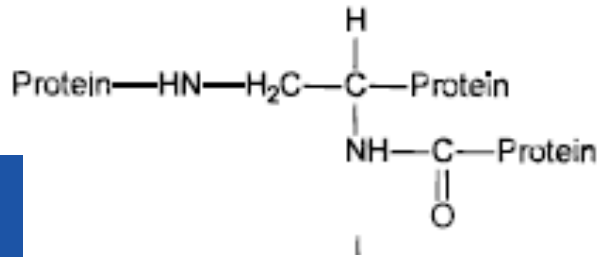
I. Olabarrieta et al., *Biomacromolecules* **7** (2006) 1657-1664.

Extracted proteins



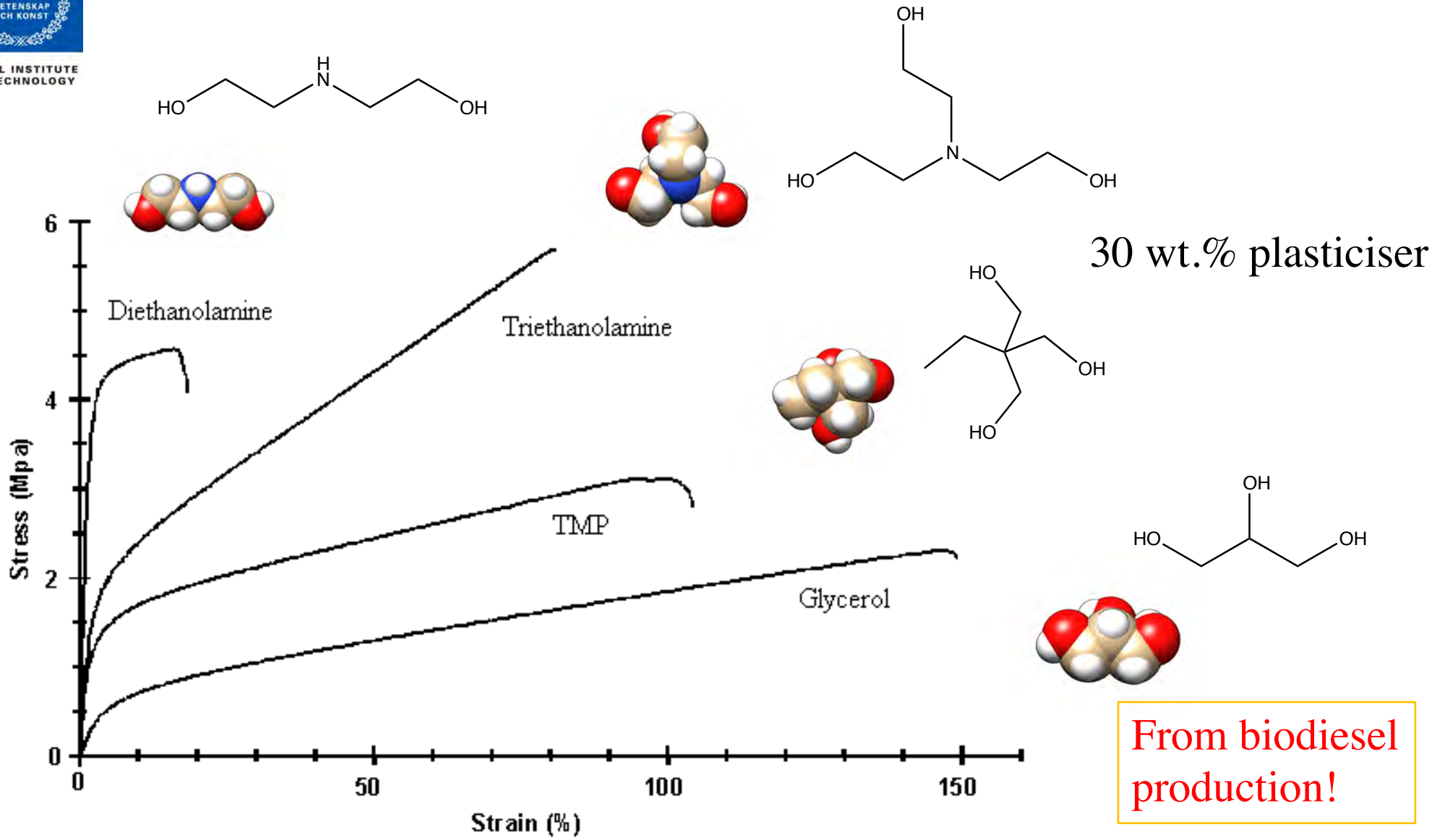
1. H_2O
2. NaCl
3. NaCl
4. Ethanol
5. 1-propanol
6. 1-propanol + DTT (reducing agent)
7. 1-propanol + DTT + acetic acid
8. SDS (secondary bonds) + DTT (100° C)
9. Urea + SDS + DTT (100° C)

Isopeptide bonds



I. Olabarrieta et al., *Biomacromolecules* **7** (2006) 1657-1664.

Tunable properties (gluten and plasticiser)

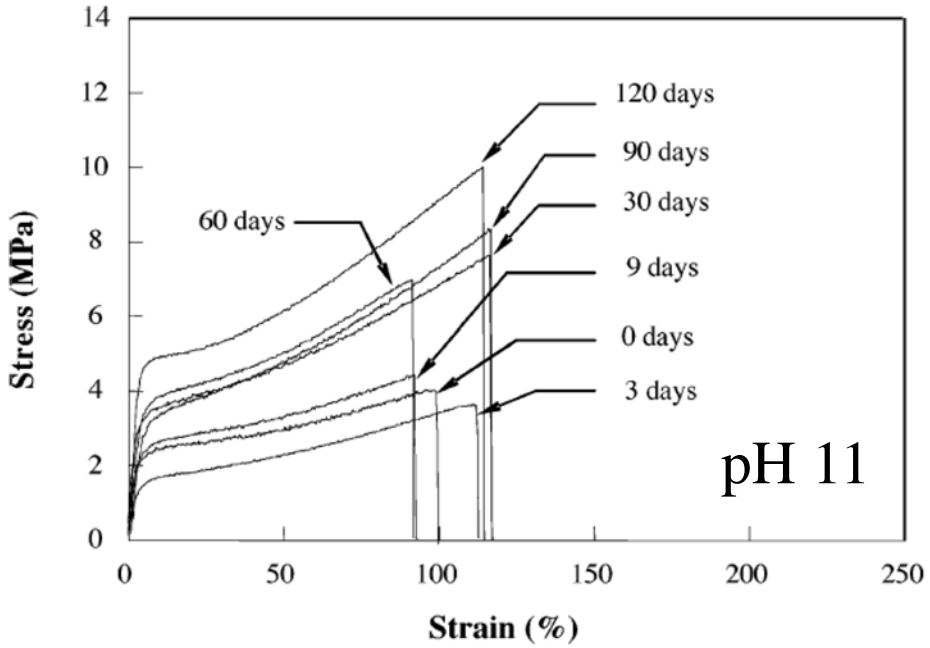


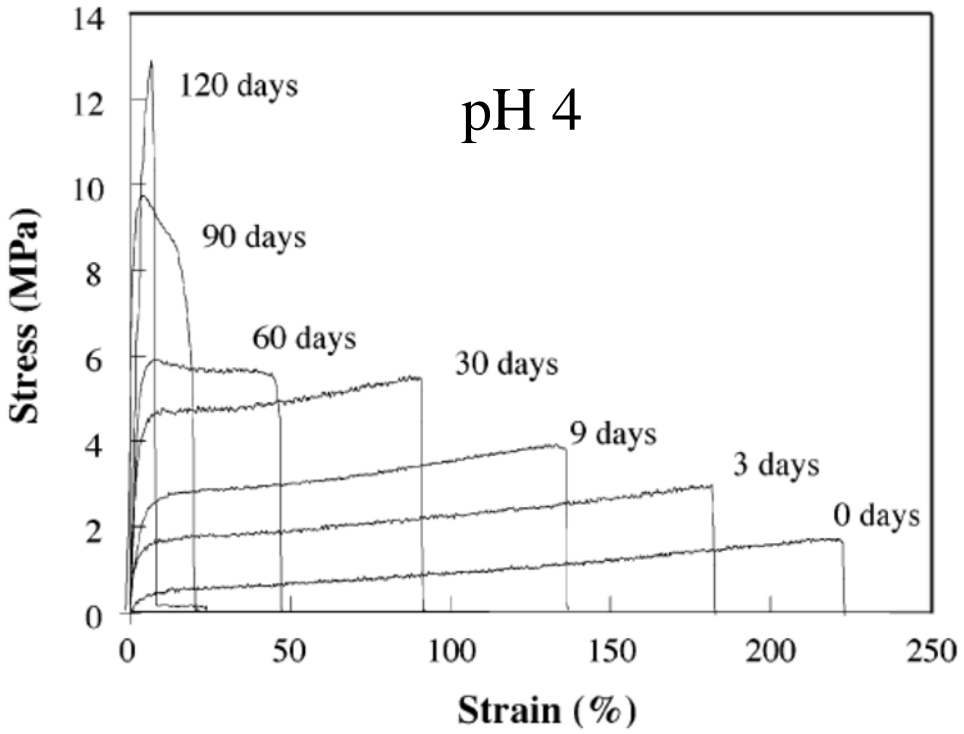
From biodiesel production!

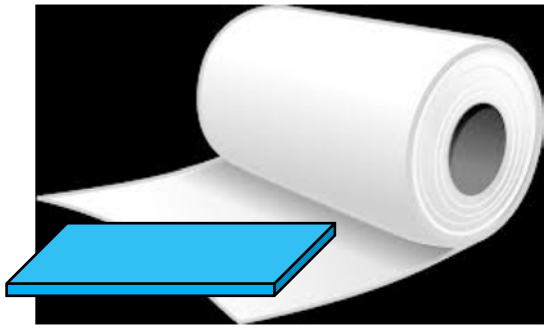
"Plasticizers for protein-based materials", Ullsten et al. in *Viscoelastic and viscoplastic Materials*, INTEC, 2016

Glycerol migration, bleeding

Gluten and glycerol

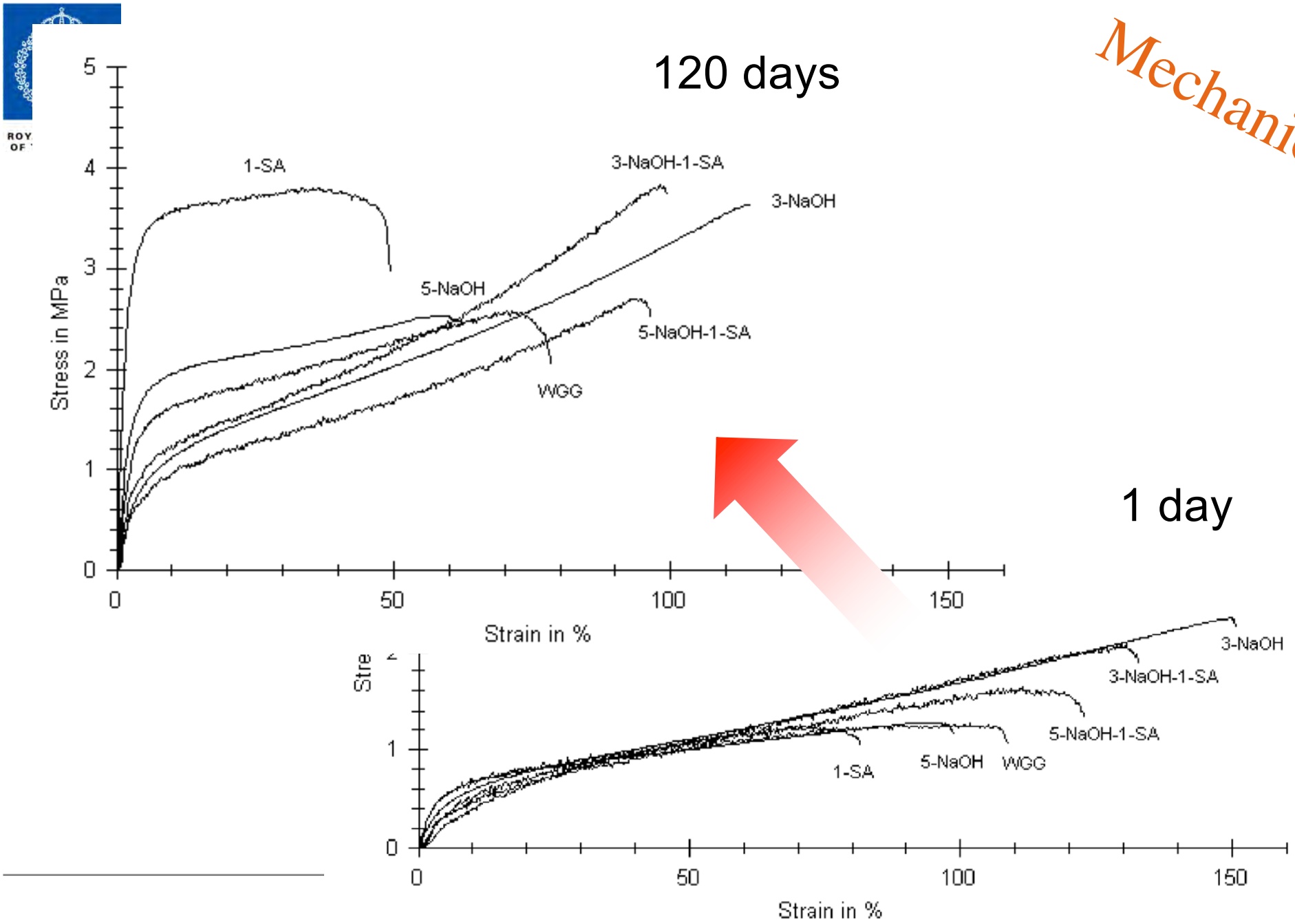






Olabarrieta et al., *Biomacromolecules* **7** (2006) 1657-1664.

Mechanics

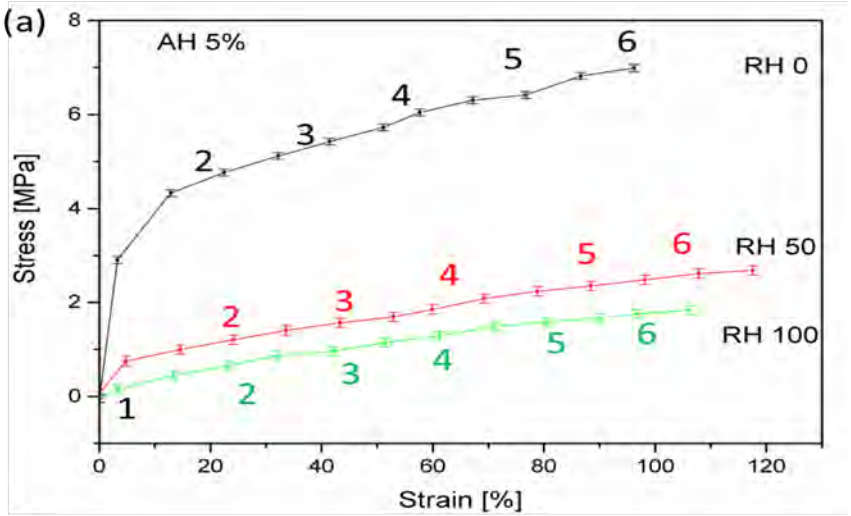


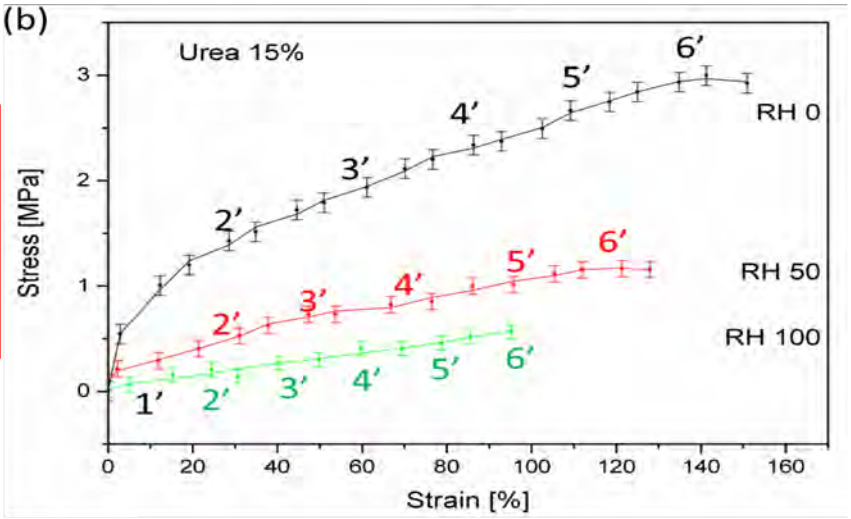
N. H. Ullsten et al., *Biomacromolecules* **10** (2009) 479-488.

Effects of moisture

Moisture content in gluten at different RH

Relative humidity [%]	Moisture content [%]					
	AH3	AH5	AH10	U10	U15	U20
0	0	0	0	0	0	0
50	9.5	9.3	9.4	10.4	10.8	11.0
100	51.6	51.0	51.4	55.6	57.5	58.9



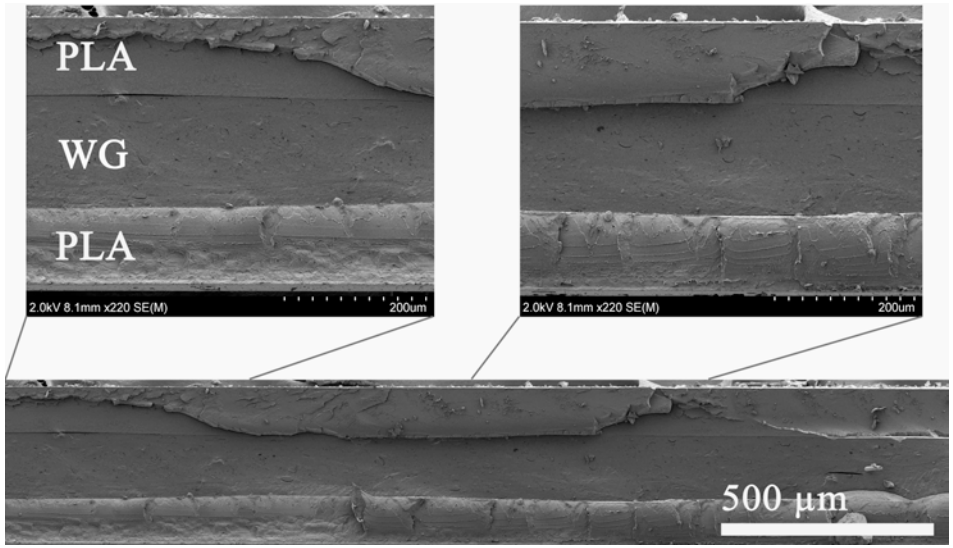


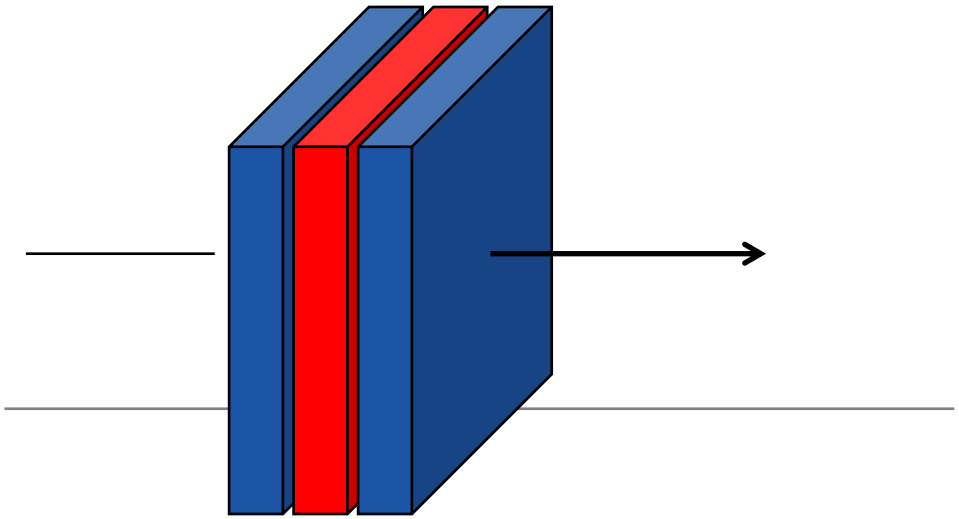
sample	OP ($cm^3 \cdot mm/m^2 \cdot day \cdot atm$) at 23 °C, 0% RH	OP ($cm^3 \cdot mm/m^2 \cdot day \cdot atm$) at 23 °C, 50% RH	WVTR ($g \cdot mm/m^2 \cdot day$) at 38 °C, 90% RH
WG-110-30	0.117/0.329[a]	7.771/8.156	OR[b]

S.-W. Cho et al. *J. Agric. Food Chem.* **58** (2010) 7344-7350.

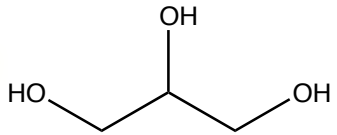
S. Yu et al. *ACS Sustain. Chem. Eng.* 2016.

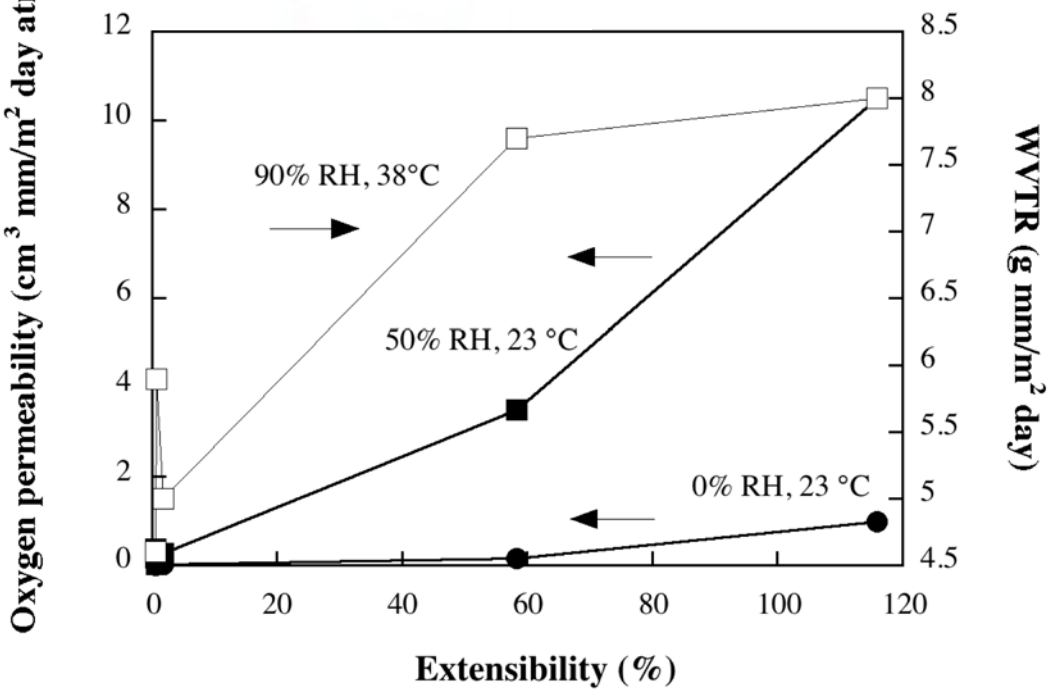
High barrier solutions





Glycerol in wheat gluten (WG)





S.-W. Cho, M. Gällstedt and M. S. Hedenqvist *J. Agric. Food Chem*. **58** (2010) 7344-7350.

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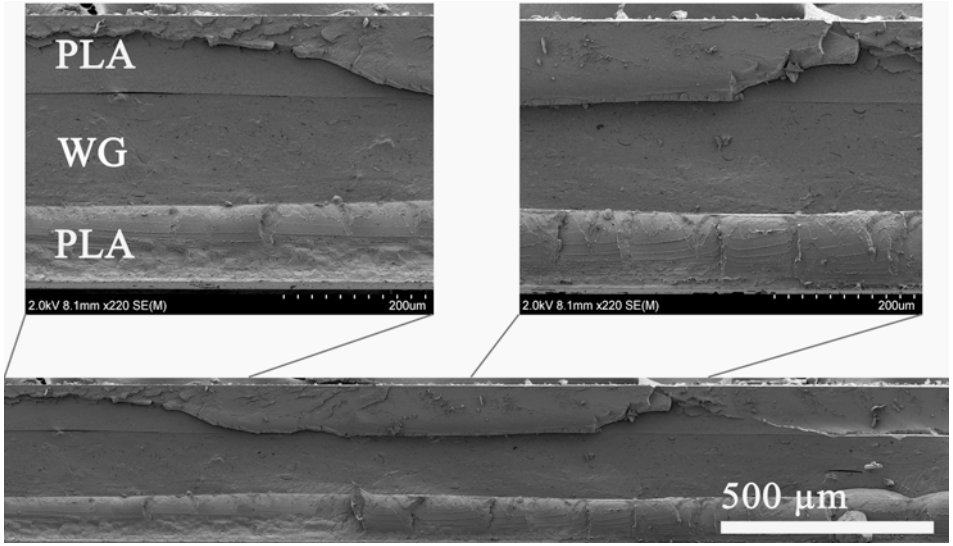
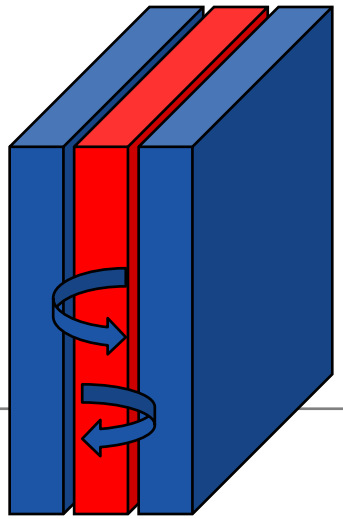
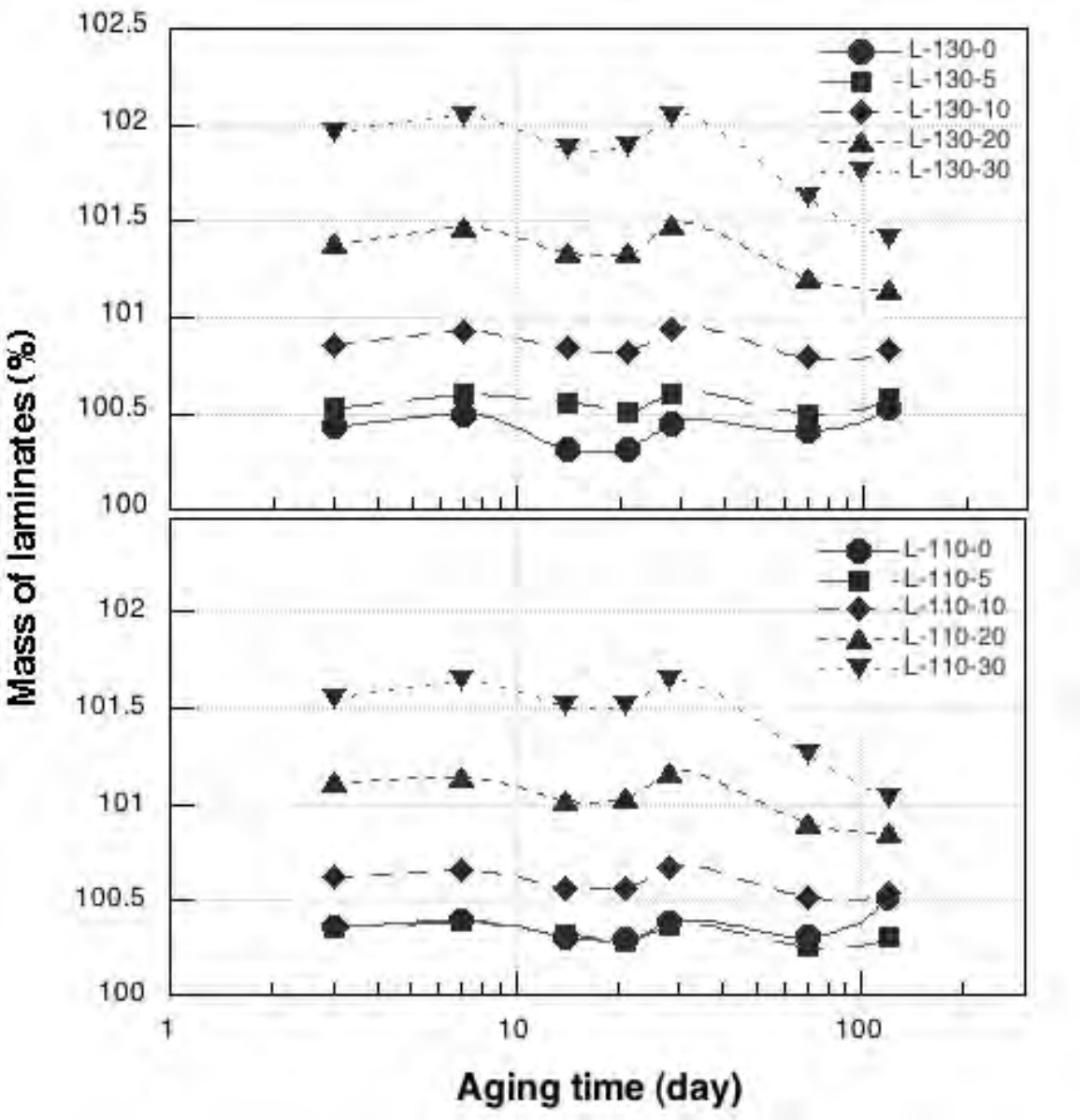
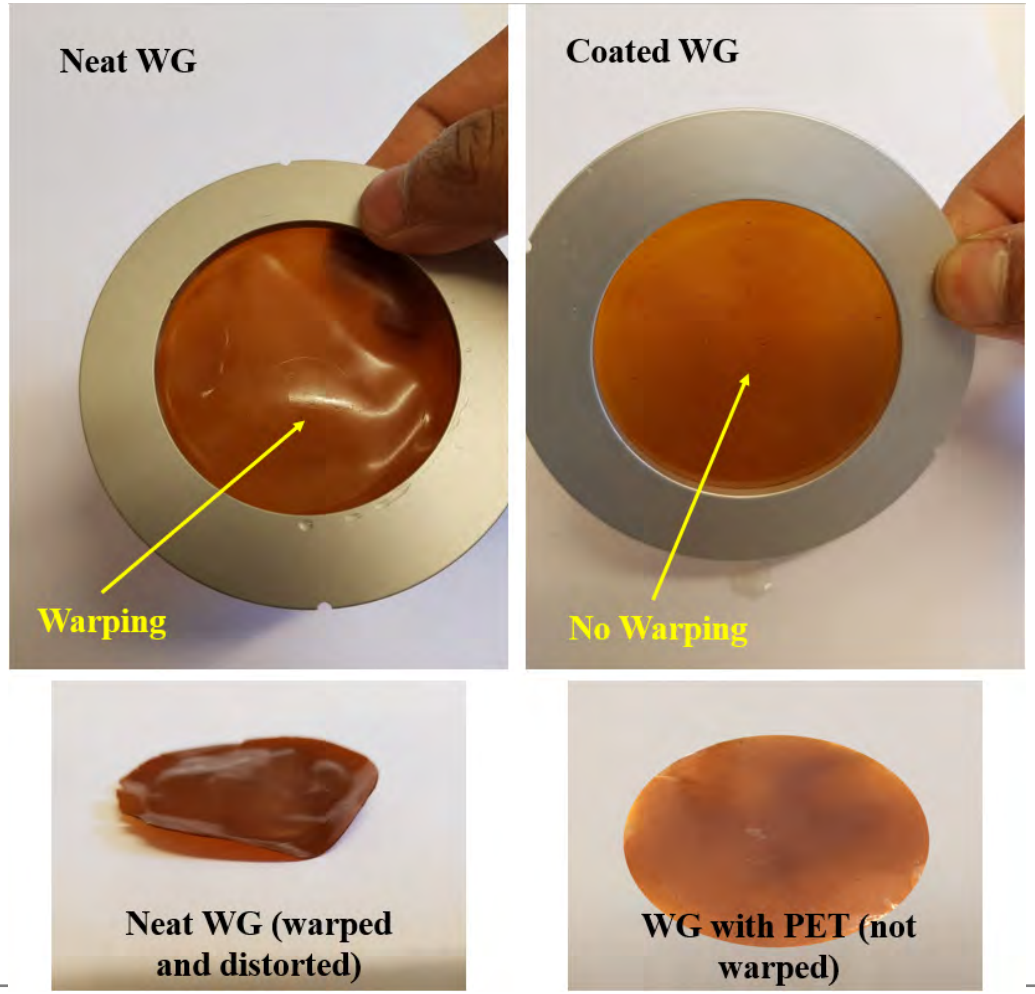
No migration







PET-coated wheat gluten

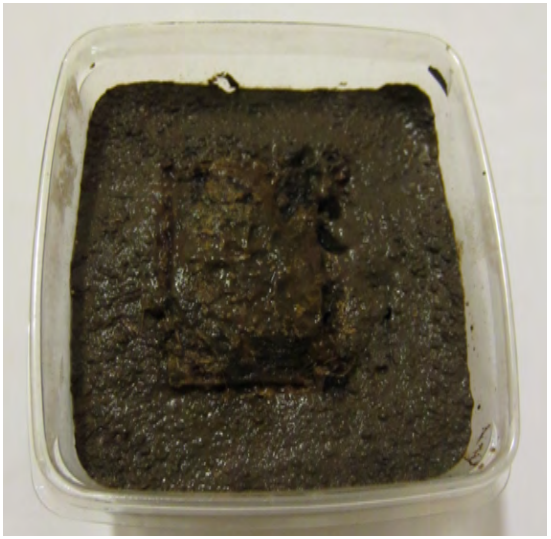


100 %/50 % RH profile

WVTR (PET)
11.2 ± 0.6 g/m^2/day

O. Das, T. A. Loho, A. J. Capezza, I. Lemrhari, M. S. Hedenqvist, *Coatings,* **8** (2018) 388-395

Biodegradation of hemp fibre-reinforced wheat gluten



Biodegradation of the composite after 45 (left) and 180 days (right). Soil for the experiment was obtained from an organically grown field situated near the Swedish University of Agricultural Sciences, Alnarp (N55.661303, E13.077222).

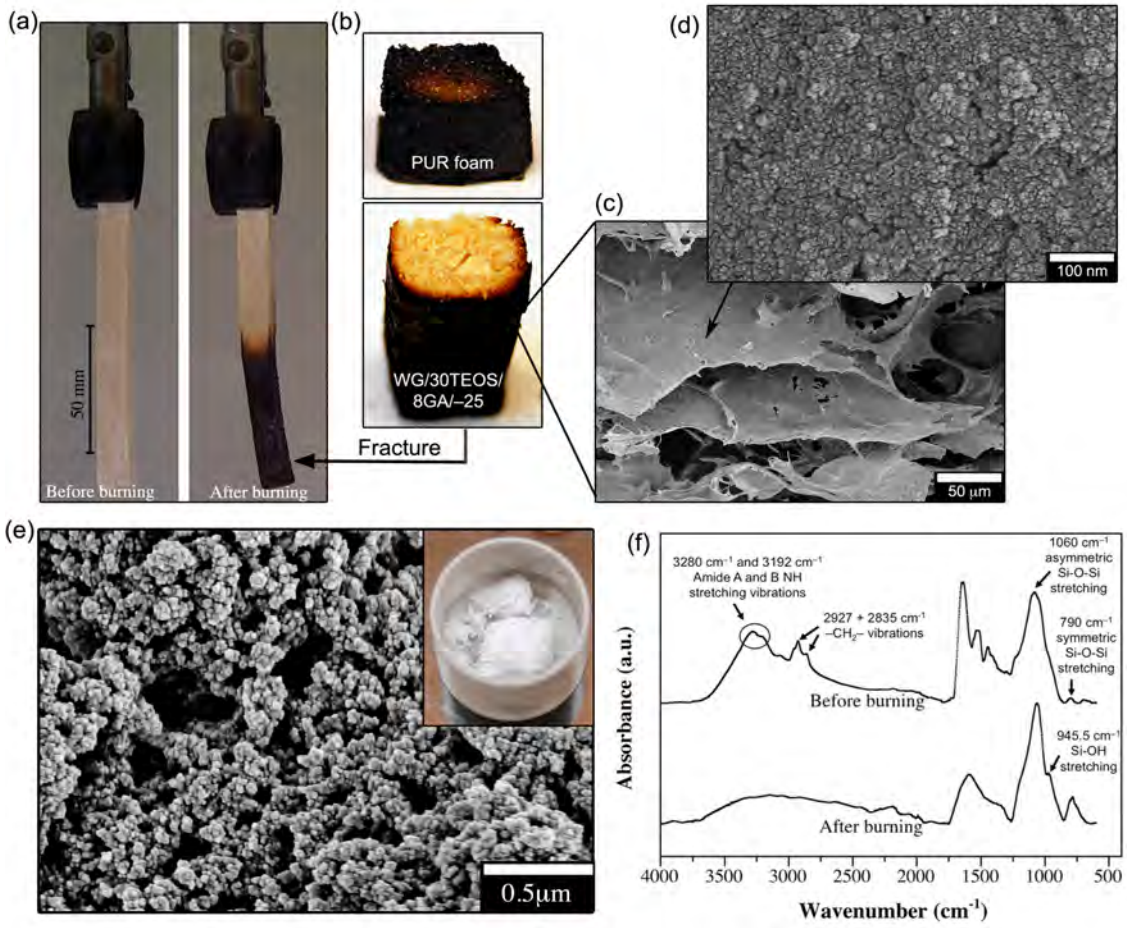
F. Muneer et al. *Bioresources* **9** (2014) 5246-5261

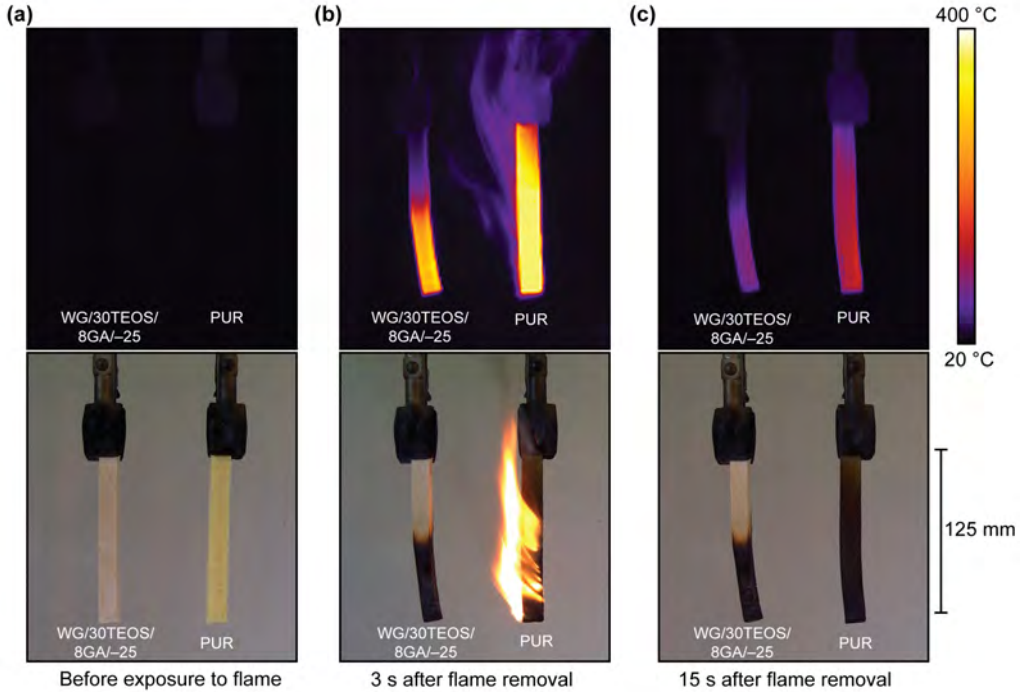
fire properties

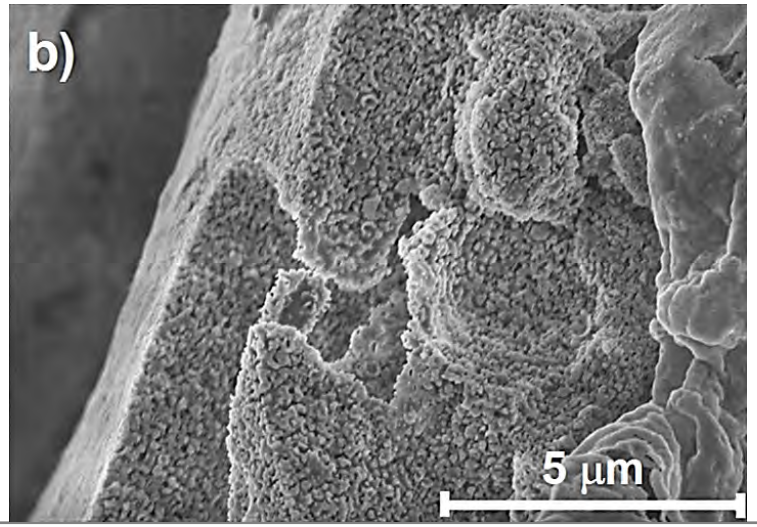
Hybrid films and foams

In-situ polymerized silica

Gluten



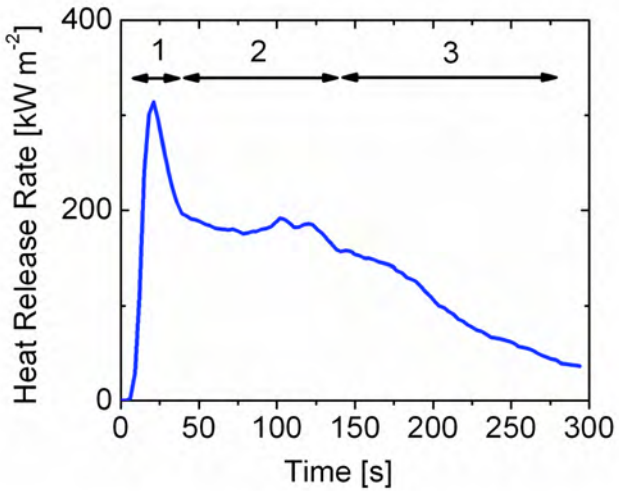




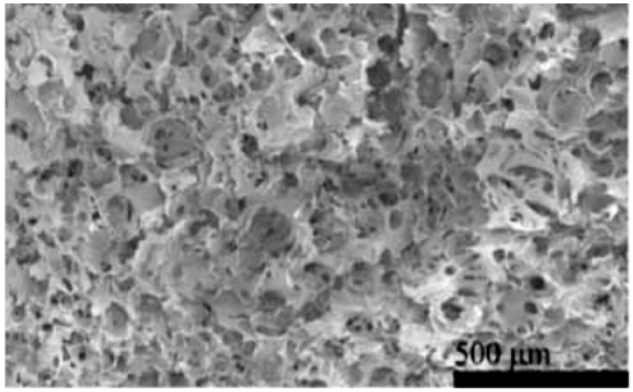
Q. Wu et al., *J. Mater. Chem. A* **2** (2014) 20996–21009.

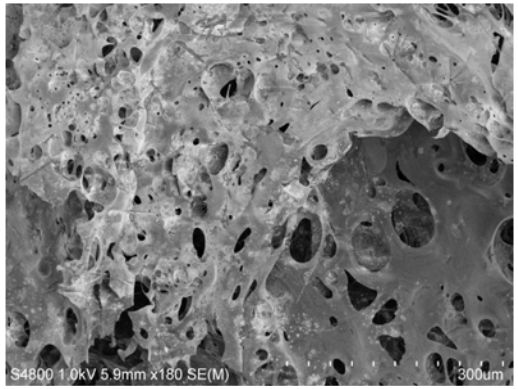
H. Türe et al., *Macromol. Chem. Phys.* **214**, (2013) 1131-1139.

fire properties



before

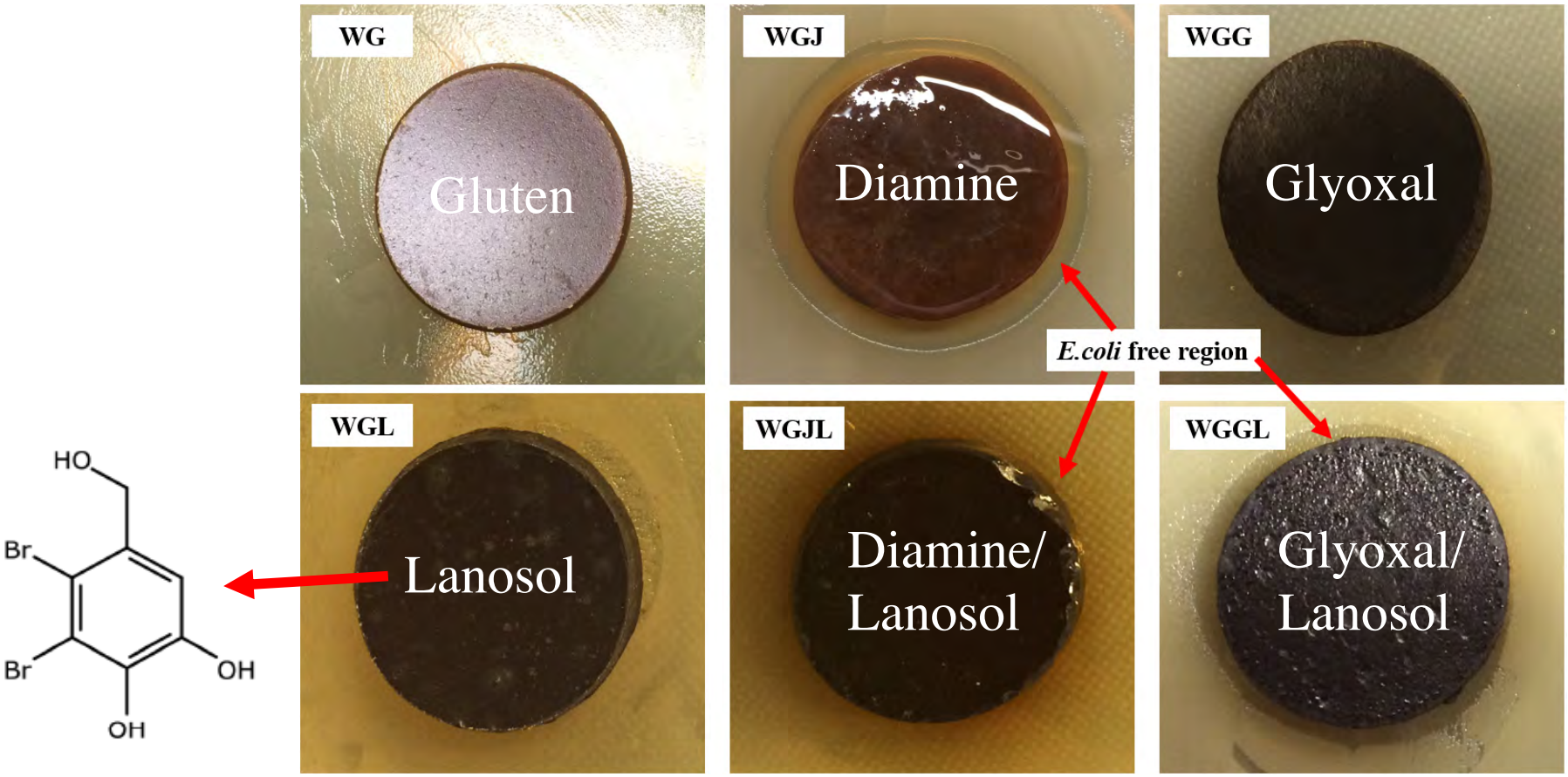




after

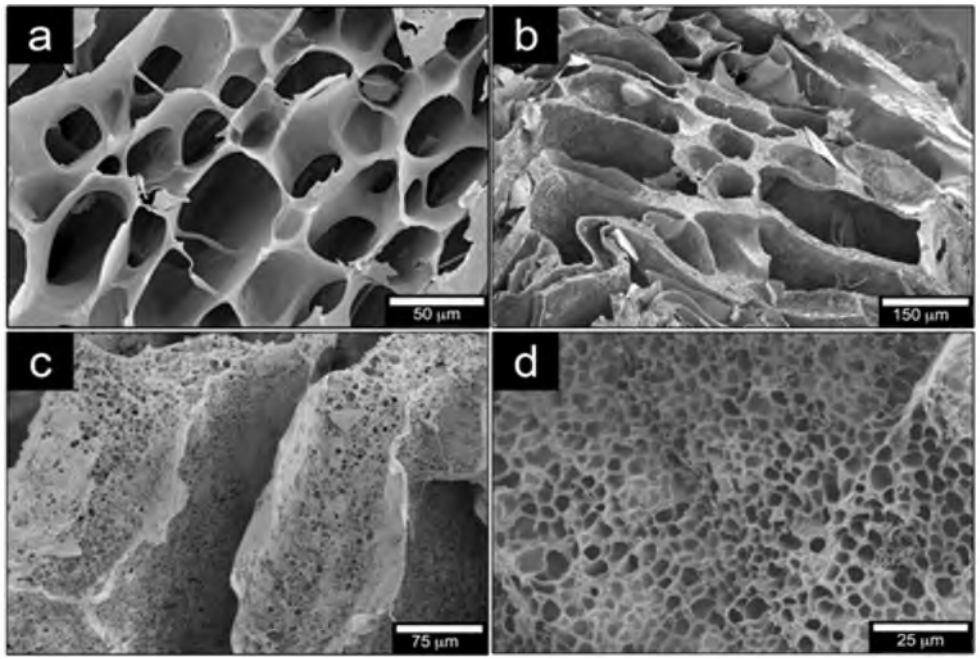
T. O. J. Blomfeldt, F. Nilsson, T. Holgate, J. Xu, E. Johansson and M. S. Hedenqvist, *ACS Appl. Mater. Interf.* **4**, (2012) 1629-1635.

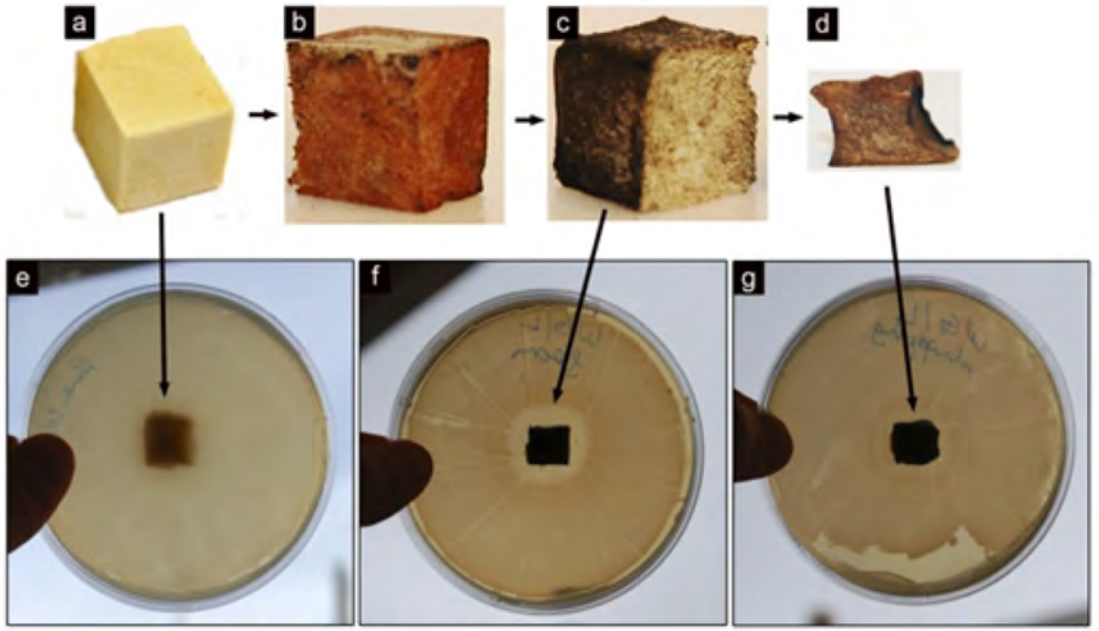
Microbe resistance using a diamine, glyoxal and lanosol



O. Das; F. Rasheed, N. K. Kim, E. Johansson, A. J. Capezza, A. L Kalamkarov, M. S. Hedenqvist, *J. Clean. Prod.*, **222** (2019) 163-173.

Bimodal pore size and antimicrobial properties





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Challenges; accelerated testing

Challenges; biobased materials

Thank you!