9th UHMWPE International Meeting

UHMWPE in Orthopaedics in 2019: Advances in Polymer Chemistry

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UHMWPE in 2019: open points?

- Unexpected oxidation of 1st generation XLPE in vivo
- Peroxides – an alternative to radiation crosslinking?
- Antioxidants: are they all the same? Mechanisms of stabilization
- UHMWPE composites: what's on?
- Drugs-eluting UHMWPE

Unexpected oxidation of 1st generation XLPE in vivo

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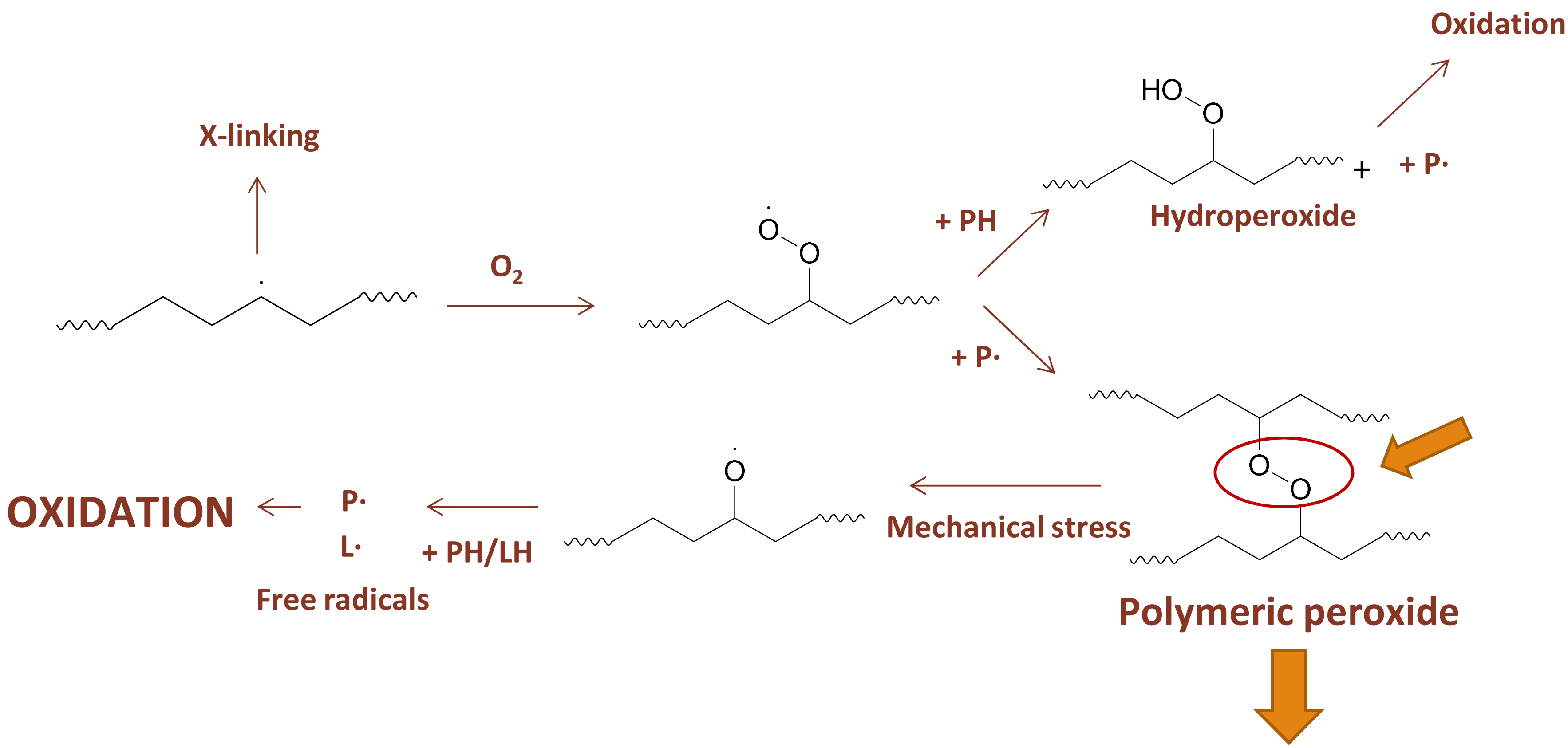
Mechanical stress + lipids absorption

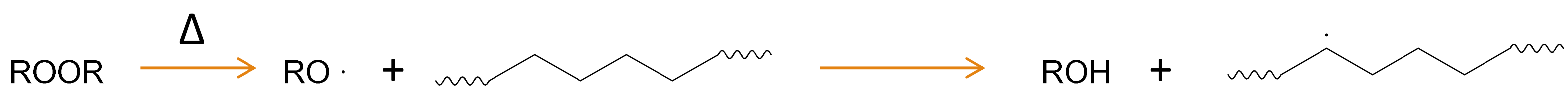
Chemical mechanism?

E. Oral et al. J. Biomed. Mater. Res. Part B Appl. Biomater. 100B (2012) 742–751
M. Regis et al. J. Mater. Sci. Mater. Med. 25 (2014) 2185-2192



- Do they survive annealing/remelting?
- Difficult to identify

Peroxides – an alternative to radiation crosslinking?



Cross-linking

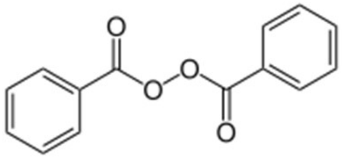
Peroxides can be incorporated

during consolidation (blending)

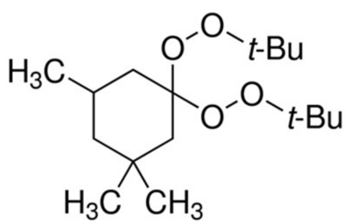
- Cross-linking of the molten polymer
- Uniform distribution of cross-links all over the polymer bulk

in the end-product (diffusion + thermal treatment)

R.M. Gul et al J. Orthop. Res. 35 (2017) 2551–2556; E. Oral et al J. Orthop. Res 37 (2019) 2182–2188;
P. Bracco 7th UHMWPE meeting (2015), P. Bracco 8th UHMWPE meeting (2017)

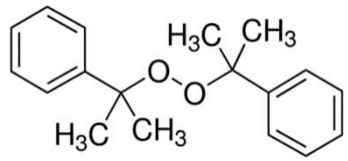


Dibenzoyl peroxide

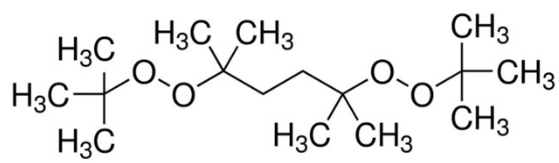


1,1-di(t-butylperoxy)-3,3,5-trimethylcyclohexane

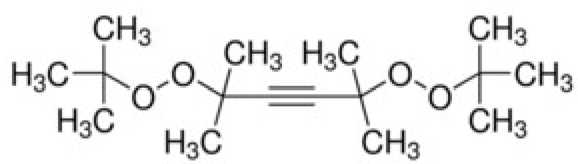
Decomposition temperature



Dicumyl peroxide



2,5-dimethyl-2,5-di(t-butylperoxy)hexane



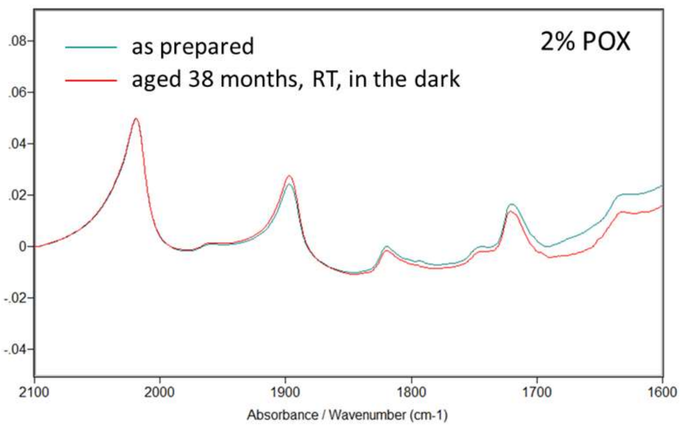
2,5-dimethyl-2,5-di(t-butylperoxy)-3-hexyne

Decomposition temperature

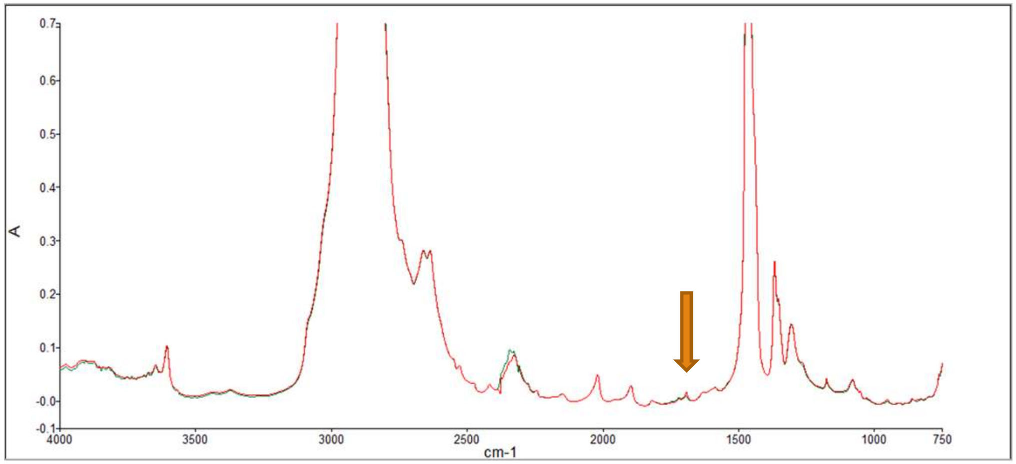
Pros & cons

- Residual by-products → Volatile/biologically safe*
- Oxidation stability? → Antioxidants

POX and POX/MPW cross-linked UHMWPE
Real time ageing



FTIR
Dicumyl peroxide – before vs. after aging

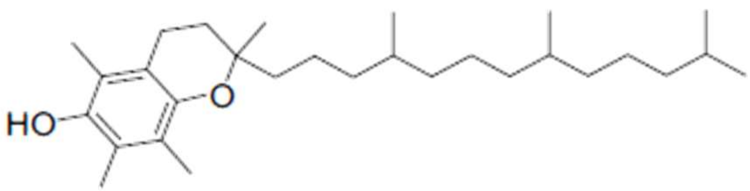


- Avoids radiation cross-linking step
- Versatility: choice of the appropriate peroxide (T_d)/ concentration/incorporation method

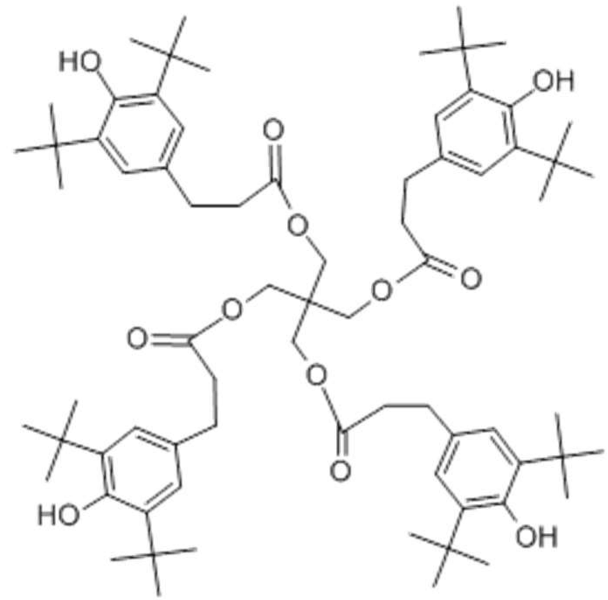
*D.A. Bichara et al J. Arthroplasty. 33 (2018) 2666–2670

Antioxidants: are they all the same?

HINDERED PHENOLS

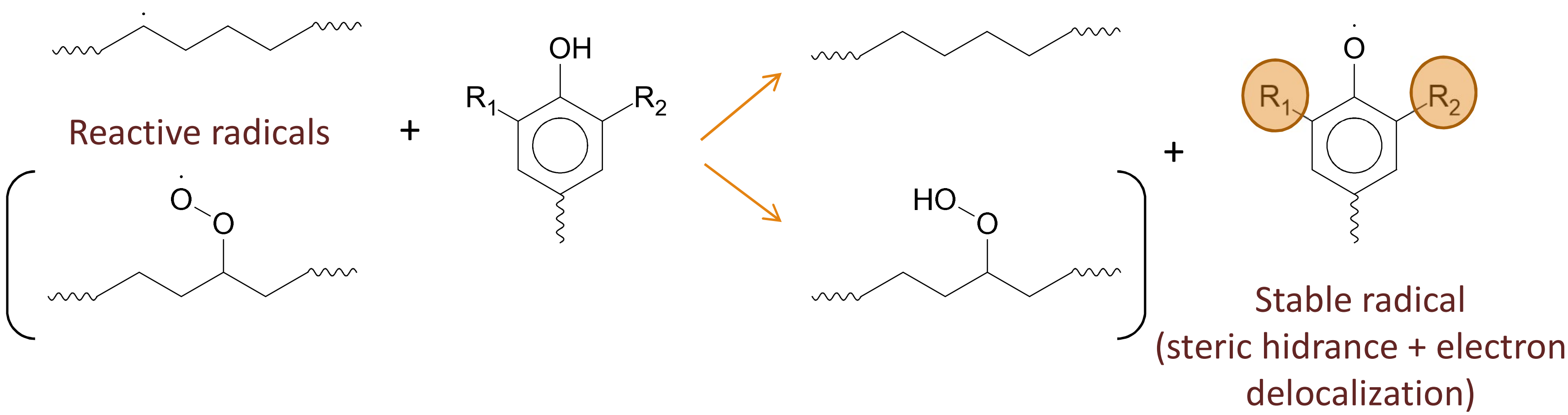


α-tocopherol (vitamin E)



Pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate) - PBHP

Hindered phenols: primary mechanism of stabilization

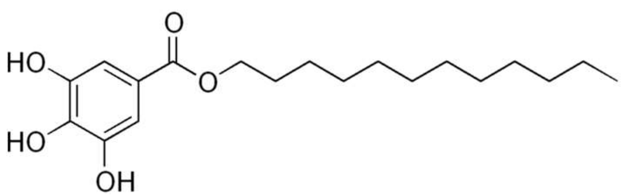


Comparisons?

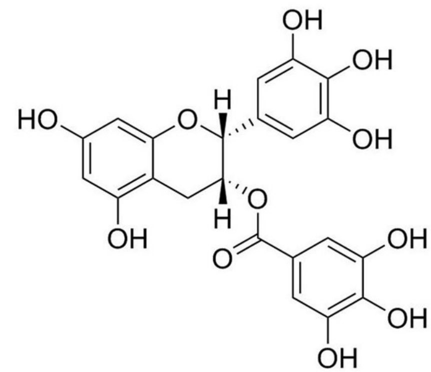
- MOLAR concentrations /different mobility (solid phase)
- Appropriate testing methods

Proven efficiency in clinical use

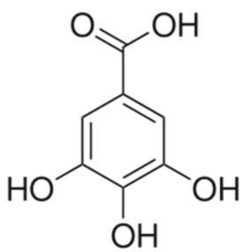
NATURAL POLYPHENOLS



Dodecyl gallate



Epigallocatechin gallate



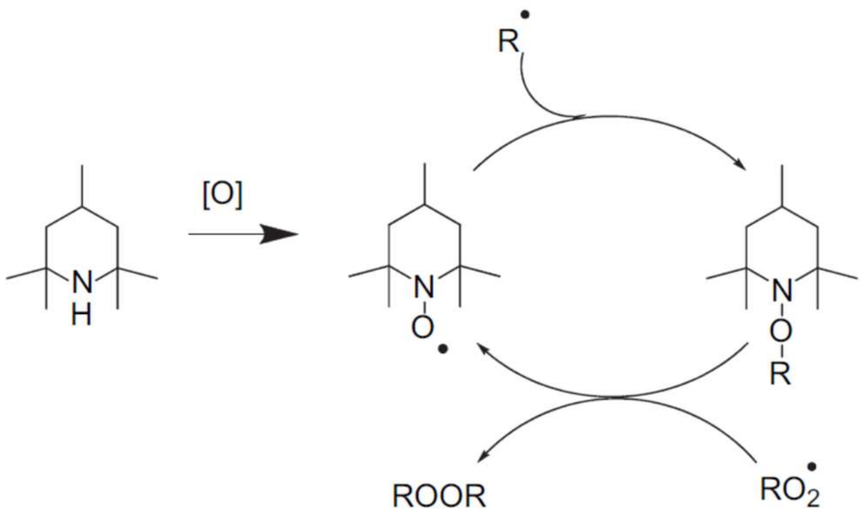
Gallic acid

The radical stability is due to electron delocalization only

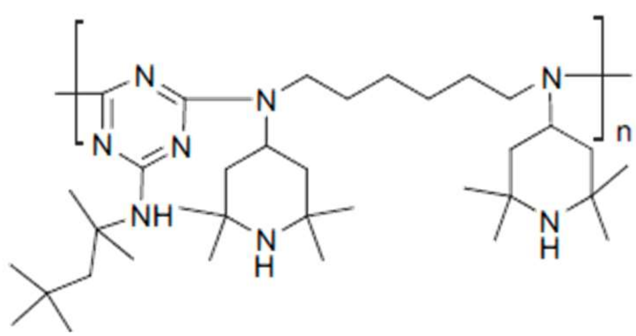
J. Shen et al Polym Degrad Stab 105 (2014) 197–205
Y. Ren et al. Mater. Sci. Eng. C. 94 (2019) 211–219

HALS (hindered amines light stabilizers)

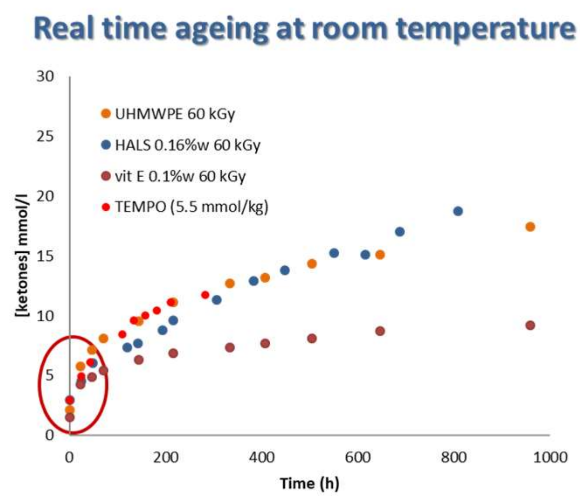
Hindered amines: mechanism of stabilization



Chimassorb 944



Gjisman, P et al. Biomaterials 31 (2010) 6685-6691



P Bracco, 6th UHMWPE meeting, 2013

UHMWPE composites?

Advancements in processing technologies, sterilization methods, packaging solutions, etc

UHMWPE/Hydroxyapatite

Goal: to achieve better dispersion of HA for increased mechanical properties

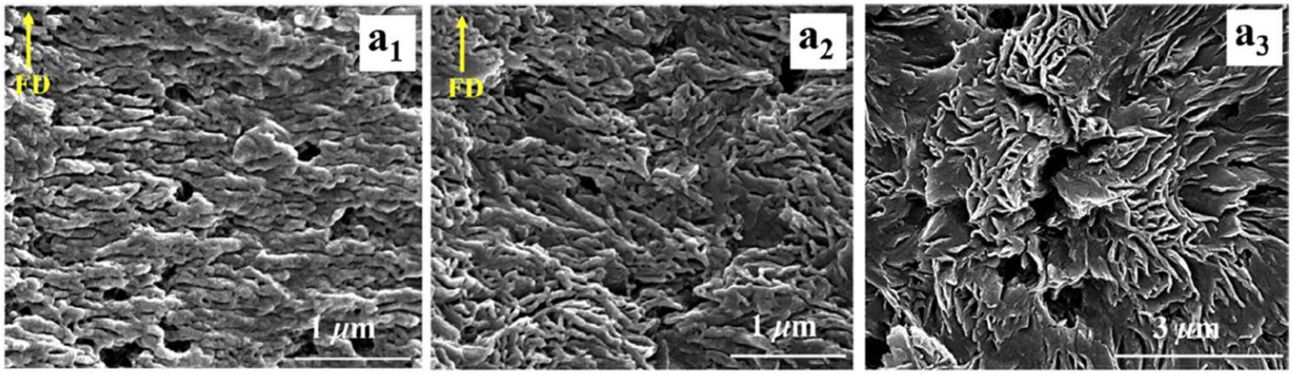
Bioactive polyethylene composites

UHMWPE/hydroxyapatite (HA) biocomposites with bone-like structure

- UHMWPE/HA (+10 wt% ULMWPE as flow accelerator) direct melt compounding in a twin-screw extruder
- extruded pellets processed by oscillation shear injection molding (OSIM) machine
- the melt is injected into the mold and forced to move repeatedly in a chamber by two pistons that move reversibly as the solidification progressively occurs from the mold wall to the core

Y.F. Huang et al. Compos Sci Technol 151 (2017) 234–242

Gradiently oriented architecture: in the **outer layer**, the shear induces **highly oriented UHMWPE** lamellae, which mimic the aligned collagen fibers in the natural bone. In the **inner layer,** chain relaxation gives rise to **relatively disordered lamellae**, contributing to a tough core that shares the similarity with the soft internal layer of natural bones



- Improved UTS (63,4 MPa) and Impact strength (104 kJ/m^2) vs. UHMWPE/HA composites
- Good biocompatibility (osteoblast-like cells)
- Increased ability to induce hydroxyapatite formation on the surface

→ Promising candidate of replacements for cortical bones

HA/graphene nanoplatelets (GNP)/UHMWPE composite for hip implant liners

Preparation by ultrasonication/solvent mixing, followed by hot pressing

10 wt % HAp + 0.5 wt% GNP showed:
- Increase in elastic modulus and yield strength
- Decrease in wear rate and coefficient of friction, compared to pure UHMWPE

→ nucleating effect of GNPs (critical dose)

HAp particles were successfully capable of decreasing cytotoxic effect of GNPs (MG-63 cells)

S. Mohseni Taromsari Compos. Part B Eng. 175 (2019) 107181

UHMWPE/CNT

Biocompatibility?

MWCNT/UHMWPE nanocomposites (0.05 - 5.0 wt %)
prepared by ultra-sonication/mixing/hot pressing.

Increase in crystallinity and tensile properties
(yield and tensile strength, elastic modulus)

Biocompatibility tested using human fibroblast cell lines → Up to 80% increase of cell viability for MWCNT composites, compared to neat UHMWPE.

↓

Increased roughness of the MWCNT/UHMWPE composites stimulated cell growth

N. Mamidi et al. J Biomed Mater Res. A. 105 (2017) 3042–3049

CNTs as reinforcement of porous UHMWPE for drug delivery

0.1 wt% of high aspect ratio CNTs reinforced UHMWPE composite prepared by pressing composite powders at 300 MPa at RT + curing at 160 °C, 60 min

Modified chemical etching (boiling xylene), followed by lyophilization

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Interconnected micro pores on PE surface

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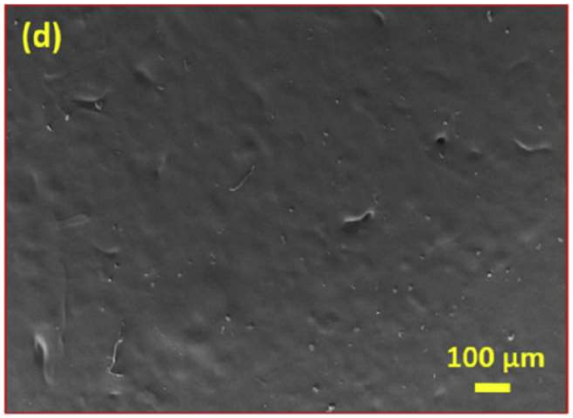
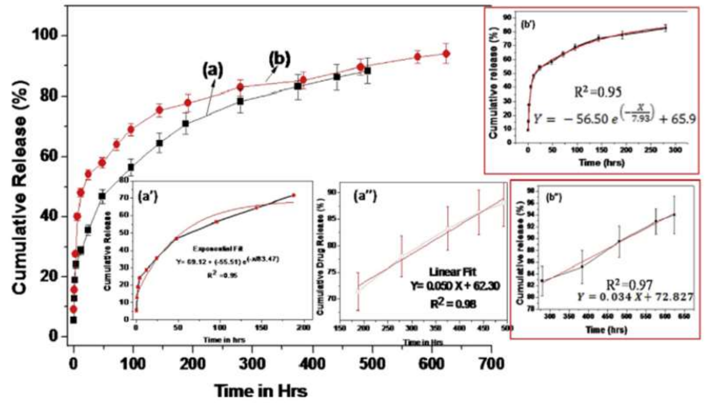
Impregnated with gentamicin loaded chitosan solution →



R. Manoj Kumar et al. J Drug Deliv Sci Technol. 52 (2019) 748–759

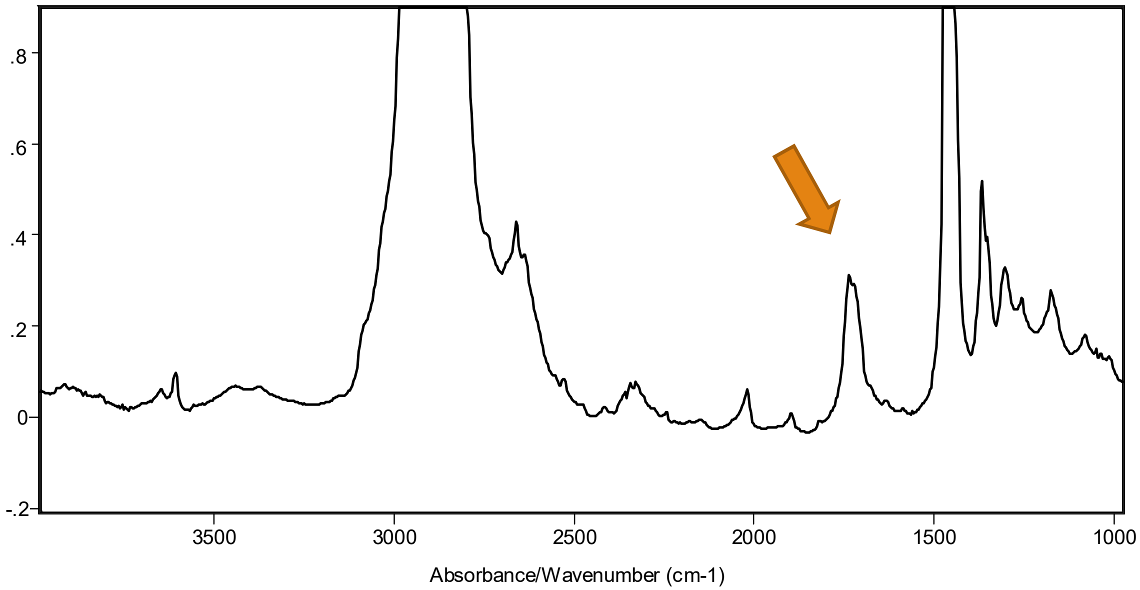
- Homogeneous CNTs dispersion
- Increase in cristallinity (CNTs)
- Decrease in friction coefficient and specific wear rate (ball on disc tribometer) before and after drug elution
- Increased hardness and modulus (microindentation) before and after drug elution

Burst + sustained gentamicin release (up to 490h)



Antibacterial properties successfully tested vs. S. aureus

Survival and proliferation of MG-63 cells confirm cytocompatibility



Hip liner, retrieved in **2017 (US)**, time in vivo **4y**

OI = 2.7

ADVANCES IN UHMWPE?

THANK YOU

Open for registration: https://sciforum.net/conference/polymers2020