Aqueous Nanodispersions of Biodegradable Polyesters for Nanofiber Preparation by Electrospinning

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From water processable to water stable

Biodegradable Polyesters

Water stable???

Nanomaterial

Processing from water
The vision
Protection by mating disruption with pheromones from artificial dispensers

Requirements
- Dispensers have to create homogenous pheromone cloud
- Dispensers have to be biodegradable
- Dispensers have to be stable during release of pheromone - suspension electrospinning
- Dispensers have to release pheromone steadily
The concept
Use of electrospun pheromone releasing nonwovens

Pheromone releasing microcapsules

Nanofiber nonwovens

The green approach
• Water based formulation
• Water stable nonwoven
• Degradable nonwoven
• Pheromone release
In brief about nonwovens by electrospinning
A coating technique

Fiber diameters 1 – 10,000 nm
From lab scale to technical scale
Take home message
So many options by electrospinning
for novel nanofiber nonwovens

Reviews:
Greiner, Wendorff, Angew. Chem. Int. Ed. 2007, 46, 5670
Agarwal, Wendorff, Greiner, Polymer 2008, 49, 5603 (Biomed.)
Agarwal, Wendorff, Greiner, Macromol. Chem. Rapid Commun. 2010, 31,
Nanofiber nonwovens

Pheromone releasing
Microcapsules
How to electrospin for water stable biodegradable polymers from water?

Well established biodegradable polymers: Aliphatic polyesters (polylactide, PCL...)

Problem: soluble only in hazardous solvents
No electrospinning on fields possible

The possible solution: Suspension electrospinning of secondary suspensions of biodegradable polyesters
How to get secondary suspensions of biodegradable polymers?

Water soluble block

Biodegradable hydrophobic block

Suspensions by micell formation

H₂O
Synthesis diblock copolyester

\[ \text{HO} \rightarrow \left\{ \begin{array}{c} \text{HO} \\
\text{OH} \end{array} \right\} \]

\[ M_n = 6400 \text{ (GPC - PS standards } M_w / M_n = 2.1) \]

Insoluble in water

\[ T_m = 58 \, ^\circ\text{C} \]
Secondary dispersion of the diblock copolyester in water

Follow protocol of solvent displacement method
- Dissolve polyester and Brij78 (10%) in actone
- Add water
- Apply ultrasound

Stable suspension
Solid content: 2.5%

Too low for electrospinning

Size Distribution by Intensity

112 nm
Up-concentration of the secondary dispersion

Dialysis of suspension

Set-up of dialysis

Dialysis tube

Suspension of polyester

Water + PVA(16%)
Up-concentration of the secondary dispersion

Dialysis of suspension

Stable suspension

Solid content: 16%

Good for electrospinning

Size Distribution by Intensity

109 nm
Take home message

Aliphatic water insoluble polyesters can be dispersed in water up to 20 %
Concept for submicron fibers by suspension electrospinning

Stoiljkovic et al., Polymer 2007, 48, 3974
Stoiljkovic et al., Macromolecules 2009, 42, 6147
P. Bansal et al., in prep.
Electrospinning of up-concentrated secondary dispersions

+3 % PEO
Electrospinning

Fiber diameter
300 - 500 nm

J. Sun, K. Bubel, F. Chen, T. Kissel, S. Agarwal, A. Greiner,
Water treatment of electrospun fibers of secondary dispersions

Water-stable electrospun biodegradable fibers from aqueous secondary dispersions

As-spun

Polyester+PEO+Brij78
No suspension particles visible

After water treatment for 2 days

Slight reduction of fiber diameter
No Brij78 and PEO left
How about the biodegradability

![Chemical structure]

- Fast enzymatic degradation
- Slow hydrolytic degradation
- Low cytotoxicity (without tenside)

![Graph with data points and trend lines showing weight loss over time with and without enzyme.]

F. Chen
Y. Zhang
Take home message

Electrospinning of secondary dispersions of alipahatic polyesters results in water stable biodegradable nanofiber nonwovens.
Nanofiber nonwovens

Pheromone releasing Microcapsules???
Water dispersed phermone filled microcapsules

Requirements for microcapsules
- Uptake of large amount of hydrophobic pheromone
- Microcapsules should be biodegradable
- Microcapsules should allow release of pheromone
- Microcapsules of should be well dispersable in water
Water dispersed phermone filled microcapsules

The hypothesis
Oligolactides with hydroxy/carboxylate end groups will fulfill all requirements for water dispersion and biodegradability

The answer: It is wrong

New hypothesis
Pheromone will act as hydrophob and thereby stabilize dispersions

The answer: It is right
The observation

Stable dispersions OLA with pheromone
No stable dispersions of OLA alone

Intensity Distribution

OLA/pheromone/BrijS2O
10 / 10 / 1 %

P. Bansal
Take home message

Dispersions of OLA are only Stable up to 10 % with pheromone as stabilizer!!!
How to measure dispenser efficiency on field?

Cage with lonely female beatle—how many male will visit here? Ass less as better for us – Quantification!

Nonwoven with pheromone
Pheromone release is not yet retarded enough

Take home message
- Biodegradable polyester nanoparticle dispersions up to 20%
- Biodegradable water stable polyester nanofibers from water
- High solid content OLA microcapsules dispersion with pheromones

Our serendipty will continue
Support: University of Marburg, DFG, BMBF, BLE, BASF

The teams: Agarwal and Greiner group

Partners - Profs: S. Agarwal, J. H. Wendorff, G. Leithold
Support: University of Marburg, DFG, BMBF, BLE, BASF

Poster D-PO4-27: Thermo- and photoresponsive Nanomats by Electrospinning…..
(Agarwal / Brandl) – today afternoon only!!!

We do not risk because it is difficult - It is difficult because we do not risk

Seneca