Improving the properties of biobased PLA matrices by addition of surface treated nano- and microscale particles

M. Wanner, M. Entenmann, K. Krawczyk, P. Keller, H. Greisiger, K. Er, T. Schauer
Fraunhofer Institute for Manufacturing Engineering and Automation IPA, Stuttgart

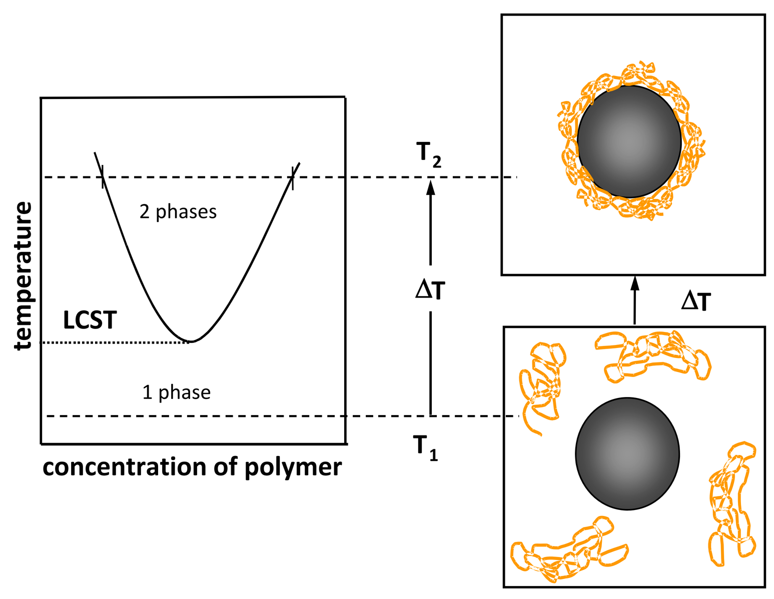
State of the art

- Polylactide acid (PLA) represents a biobased polymer with promising economic perspectives [1]. Due to its high elastic modulus, low oxygen and odour permeability, good printability, and high scratch resistance (SR), it is increasingly used e.g. in food and cosmetics packaging.
- In contrast, properties like:
  - ➔ Water vapour permeability (WVP)
  - ➔ Photodegradation resistance (PDR)
  - ➔ Antistatic, represented by the specific surface resistance (SSR)

  do not yet meet all the demands of the applicants.
- Due to decreasing price; the market acceptance of PLA will surely raise, if the critical properties of PLA could be improved economically.

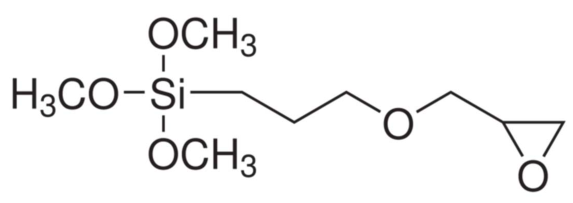
Research ideas

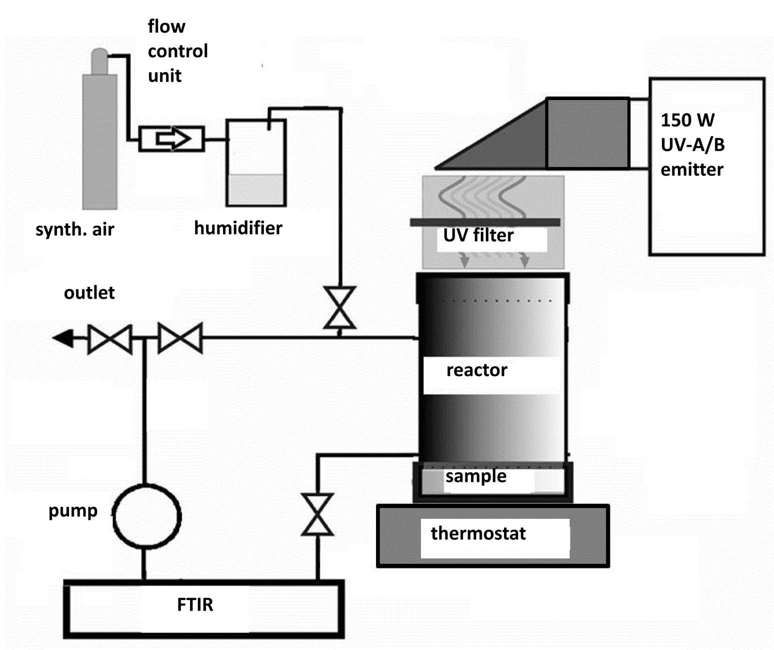
- Addition of commercially available supplies:
  - ➔ Careful market search and selection of barrier pigments and functional additives
  - ➔ Systematic and quantitatively varying addition of promising and economically acceptable products to PLA
  - ➔ Characterization of the modified films
- Additional improvement of properties by surface treatment of functional particles:
  - ➔ Generation of hydrophilic/-phobic surfaces and different extends of particle stratification by systematic variation of the silane/diole-component ratio [2]
  - ➔ Characterization of the modified films

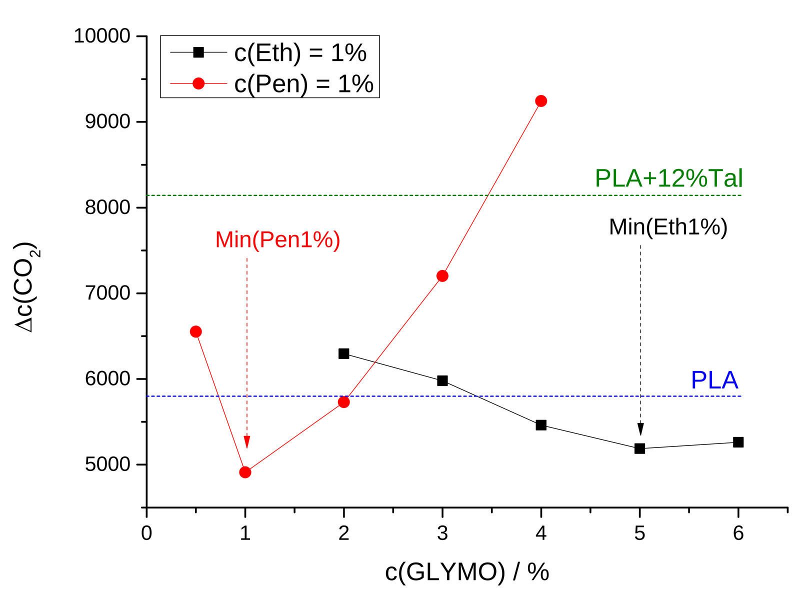


Achievements (implementation)

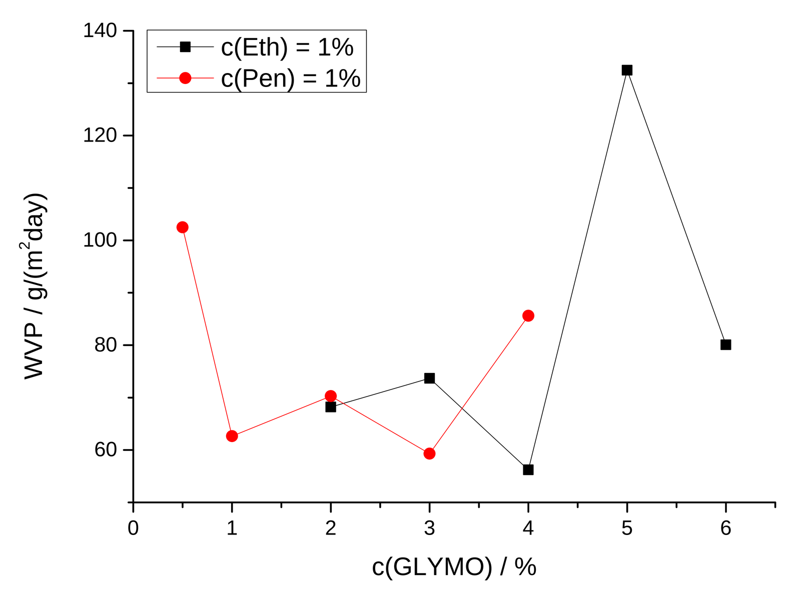
- Using talcum (Tal) as a low-priced barrier pigment, the photodegradation resistance, which is quantified by the FTIR-detected increase of $c(CO_2)$ above an UV-irradiated sample (instrumentation: see right), decreased significantly (5841 ppm → 8192 ppm)
- Two series of surface treatments using the diols ethylene glycol or pentanediol and the silane GLYMO (see below) resulted in improved photodegradation resistance (PDR) for several concentration ratios (see right).







- The best PDR Pen system (Min(Pen1%)) shows also the lowest water vapour permeability (WVP, see right). In contrast, the best PDR Eth system (Min(Eth1%)) is characterized by a very high water WVP → Only Pen is used for further optimizations.



- Using talcum as a barrier pigment, even in case of surface treatment a significant improvement of the relevant properties was not possible. Therefore talcum was substituted by Minatec 40 CM (Merck, Min) and attempts to optimize the relevant properties were undertaken by:
  - ➔ Surface treatment ; starting from the successful treatment Min(Pen1%)
  - ➔ Addition of CeO_2 nanoparticles (VP Ceria 60, Evonik); surface treatment; for improvement of scratch and photodegradation resistance
  - ➔ Addition of cellulose in order to suppress incompatibility of the surface treated pigments with the PLA matrix.
  - ➔ Addition of an organic scratch resistance additive (Byk 3239P)
  - ➔ Use of a silent crusher for a higher degree of particle separation
- The table below displays the results of the best variants regarding photodegradation resistance (PDR), reduced water vapour permeability (rWVP), specific surface resistance (SSR) and scratch resistance (SR):

Composition: PLA +	PDR $\Delta c(CO_2)$ / ppm	rWVP / µmg/(m²Tag)	SSR / Ωm	SR: 1st crack / mN
pure PLA	5981	10120	1.82 E13	35.23
12%Min	1465	2707	1.22 E7	12.37
12%Min(Pen1.0%GLYMO1.0%)	1228	1783	7.85 E14	~ 10.9
12%Min+0.2%Byk3239P with Silent Crusher	1315	2220	6.96 E12	10.70
1%f/f Ceria 60	3922	9801	7.49 E12	37.50
12%Min(Pen1.0%GLYMO0.3%) +0,3%CeO_2(Pen1.0%GLYMO1.0%)	1167	1666	1.07 E15	10.18
12%Min(Pen1.0%GLYMO0.3%) +0.3%CeO_2(Pen1.0%GLYMO1.0%Cellulose10%)	1313	1667	1.04 E13	~ 10.9

- None of the systems is best in all relevant properties
- In presence of barrier pigments no improvement of SR occurred; addition of pure CeO_2, however, resulted in better SR (and antistatic properties)
- Best antistatic properties were generated by addition of 12%Min, which also resulted in significantly improved PDR and water vapour barrier
- Addition of treated 12%Min+0.3%CeO_2 resulted in the overall best results regarding PDR as well as water vapour barrier. Antistatic properties and scratch resistance, however, are worse than in pure PLA
- Addition of treated 12%Min and 12%Min+0.3%CeO_2(treatment with cellulose) resulted in moderate but well-balanced improvements of the relevant properties. SR, however, remained low.

Next steps

- Transfer of the optimized systems to technical process:
  - ➔ Extrusion of modified PLA matrices
  - ➔ Generation of relevant technical building elements and cosmetics packaging
  - ➔ Characterization of the properties in comparison to the properties of pure PLA
- Processing of a cost-benefit calculation
- Selective implementation of economical PLA modifications in industrial processes for manufacturing biobased polymer products equipped with specific properties

References

1. Endres, H.-J., Siebert-Raths, A.; **Technische Biopolymere**, Hanser, München. 2009, 162, 348-349
2. WO 01/60926, **Method for Coating Substrate Surfaces with LCST Polymers;** WO 03/014229, **Method for Treating the Surfaces of Substrates**; WO 03/014230, **Method for Coating Substrate Surfaces**