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LOW MOLECULAR WEIGHT PLA PREPOLYMERS FOR A DIRT-REPELLENT AND FLEXIBLE VARNISH FOR PUR-BASED ARTIFICIAL LEATHER

Introduction

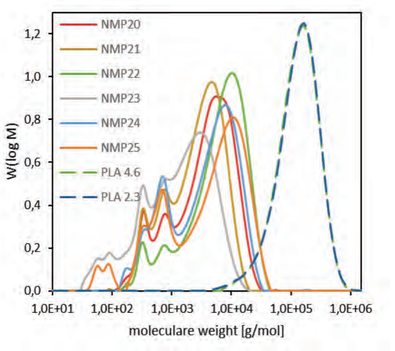
Leather, artificial leather and coated textiles are used for furniture, interior of cars, trains and cruiser ships as well as in public buildings like hotels, restaurants and hospitals. To protect the material from a wide variety of factors, they are often varnished. Protective layers based on high-molecular weight PLA-types have a high barrier effect against organic compounds such as plasticizers and dyes [1]. In order to process PLA as a varnish and to obtain a closed lacquer coat, the dispersibility of PLA in an organic solvent is necessary. Commercially available PLA types are optimized for thermoplastic processing, have high molar masses and are difficult to disperse in typical halogen-free and uncritical solvents. We have developed low molecular weight PLA prepolymers, which are dispersible in halogen-free solvents with a solid content of up to 70 % by weight and at the same time, the dispersions have a low viscosity and could be applied as a varnish for PUR-based artificial leather.

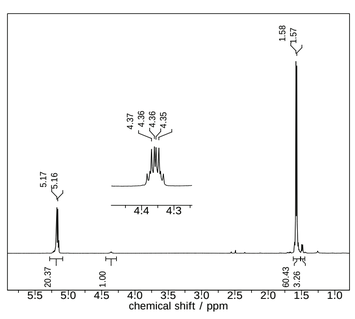
Synthesis of ...

PLA prepolymers were synthesized via condensation polymerisation of D-, L- or DL-lactic acid. We investigated the influence of synthesis parameters temperature, pressure and reaction time on the molecular weight of the PLA prepolymers during the following three steps:

Destillation	**Oligomerisation**	**Polymerisation**
100-130 °C	130-170 °C	150-170 °C
Normal pressure	Normal → 40 mbar	15-40 mbar
< 2 h	1-3 h	5-72 h

- PLA prepolymers: n up to 54 and Mw up to 7800 g/mol

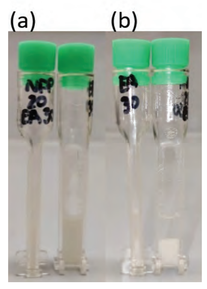


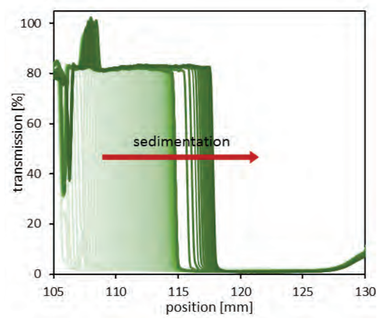


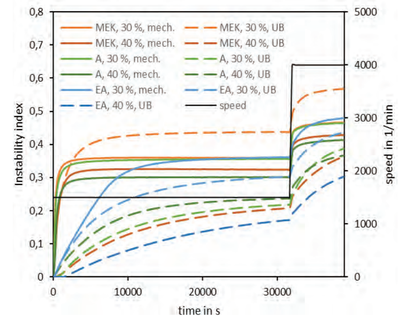
Left: Average molecular weights of selected PLA prepolymers synthesized via condensation polymerization (continuous lines) and commercial PLA types (dashed lines) measured with GPC (PS standard). Middle: ^{1}H-NMR spectrum (500 MHz) of NMP20 in $CDCl_3$. Right: Optimax reactor for synthesis of PLA prepolymers.

Dispersions of ...

Based on the calculation of Hoy solubility parameters, we picked out the following halogen-free and uncritical solvents to disperse the PLA prepolymers: acetone (A), ethyl acetate (EA), methyl ethyl ketone (MEK). We investigated the influence of various parameters on the stability of the dispersions, e.g. PLA prepolymer concentration, dispersion method (mechanical vs. ultrasound) and temperature.

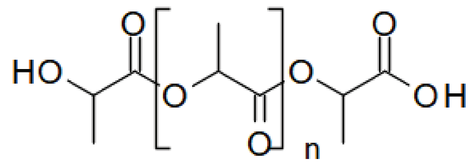






Left: Cuvettes before (a) and after (b) stability measurement. Middle: Transmission profiles of the PLA dispersion NMP20 in ethyl acetate measured by LUMiSizer (simulated time period: 270 d). Right: Instability index as a function of time for selected dispersions of NMP20 determined by SEPView 6.

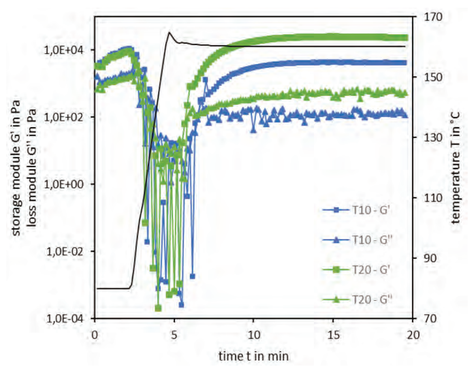
Low molecular weight PLA prepolymers

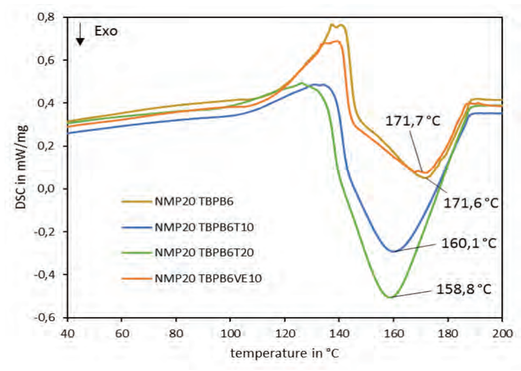


- Narrowing transmission profiles indicate compression of PLA network.
- Long-term stable dispersions were formed by ultrasound.
- High amounts of PLA prepolymer increases stability of dispersions.
- Ethyl acetate was a suitable solvent to disperse PLA.

Cross-linking of ...

We analyzed the thermal cross-linking ability of the PLA prepolymers, to ensure the formation of a closed layer of varnish.





Left: Rheological investigations of cross-linking NMP20 with initiator (TBPB) and 10 or 20 % by weight of co-crosslinker. Right: DSC measurements to investigate crosslinking behavior of NMP20 with initiator (TBPB) and without or with co-crosslinker.

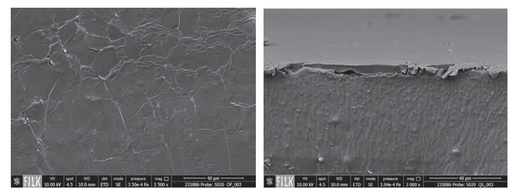
- TBPB was a suitable initiator for cross-linking of the PLA prepolymers.
- PLA prepolymers melted at temperatures around 120-140 °C and then cross-linking start at 140 °C depending on the used co-crosslinker.
- Addition of co-crosslinker reduced cross-linking temperature.
- Usual processing parameters (temperatures of approx. 160 °C) were suitable for curing the lacquer based on the PLA prepolymers.

Varnish formulation based on …

Varnishing with a spiral blade

The PLA varnishes were formulated based on the preliminary examinations. Ethyl acetate was replaced by 1,3-dioxolane for better processing. The developed varnishes were applied onto artificial leather based on PUR by spiral blade (4, 8 or 12 µm). The varnished samples were first dried at 80 °C for 1 minute and then cured at 160 °C for 3 minutes in a lab coater.

- Closed, slightly cracked, smooth and very thin (< 5 µm) lacquer layers had good adhesion to PUR.
- PLA films showed good mechanical strain and UV stability.
- PLA layers were stain-resistant.



SEM pictures of PUR artificial leather with lacquer based on the PLA prepolymer NMP20. Left: surface. Right: cross section

Results of testing mechanical stability, UV stability and resistance to soiling of the PLA prepolymer coatings (Colors of values: green – good, orange – acceptable)

	Kink	Fold	Abrasion	UV stability	Ketchup	Mustard	Red wine	Coffee with milk
	DIN 53359, 100T	DIN EN ISO 32100, 100T	DIN EN ISO 5470-2, 38,4T	DIN EN ISO 105-B02	DIN EN 20105-A03	DIN EN 20105-A03	DIN EN 20105-A03	DIN EN 20105-A03
NMP20[a]	OK	1	2	8	5	5	4-5	4-5
NMP21[a]	OK	2	3	8	4-5	4-5	4-5	4
NMP22[a]	OK	2	3	8	5	5	4-5	4-5

[a] *Condensation polymerization of L-lactic acid (NMP20), DL-lactic acid (NMP21) or D-lactic acid (NMP22).*

Conclusion

→ Moderate polymerisation temperatures, reduced pressure and long polymerisation times were optimal to synthesize low molecular weight PLA prepolymers.

→ Synthesis of PLA prepolymers with a molecular weight of up to 7800 g/mol

→ Dispersions of the PLA prepolymers in halogen free solvents had a solid content of up to 70 % by weight.

→ PLA prepolymers could be cross-linked in 2-3 minutes at usual processing temperatures of approx. 160 °C.

→ Application of the PLA varnish as thin film (< 10 µm) by spiral blade

→ Coatings with PLA prepolymers exhibited kink and fold resistance and UV stability.

→ PLA films had protective effect against everyday media.

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References
[1] Winkler, A., Trommer, K.; Coating International, 2020, 53, 28.

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