Maren Lehmann[1], Bernd Morgenstern[1],
Peter Hausoul[2], Jens Köhler[3]

FILK Forschungsinstitut Leder und Kunststoffbahnen

FURAN-BASED PLASTICIZERS FOR PVC-P

AIM

1. Synthesis and application of bio-based plasticizers as substitutes for phthalates in PVC-P
2. Development of a synthesis with high yields and multi-gram quantities
3. Creation of a plasticizer library of HMF-derivatives and study of composition-properties-relationships

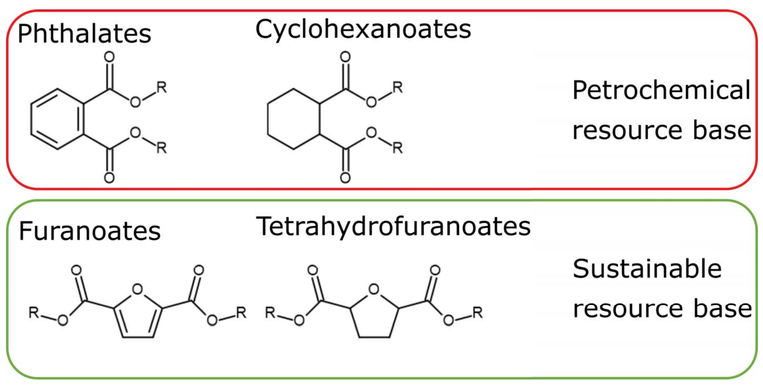

Figure 1: Structural similarities of phthalates and cyclohexanoates to the FDCA-derivatives (furanoates and tetrahydrofuranoates).

BACKGROUND

- Phthalate plasticizers: legislative registrations, increasing environmental awareness
- HMF-derivatives: structural similarity to phthalates and cyclohexanoates (Figure 1)
- 5-Hydroxymethyl furfural (HMF): one of the most promising bio-based platform chemicals, obtainable from fructose, sucrose, glucose and cellulose
- Transformation of HMF into a wide variety of derivatives: furanoates and tetrahydrofuranoates (Figure 2)
- Plasticizer properties defined by structure and composition, e.g. increasing side chain branching decreases gelling but also migration
- Plasticizer requirements: gelling at low temperatures, good solvation of PVC, high compatibility with PVC, low migration and emission, harmless to environment and humans, resistant to chemicals, heat, light and UV-radiation

MATERIALS & METHODS

- FDCA derivatives: accessible through catalytic conversion of HMF (obtainable from cellulose)
- Derivatives with side groups similar to commercial phthalates and cyclohexanoates
- Sustainable synthesis: variation in catalysts for esterification, etherification and addition reactions
- Variation of side chains: plasticizer diversity
- Study of plasticizer properties and applicability: thermal stability, gelling and solvation behaviour, migration, mechanical properties of PVC films, glass transition temperature

RESULTS (OBTAINED AT FILK)

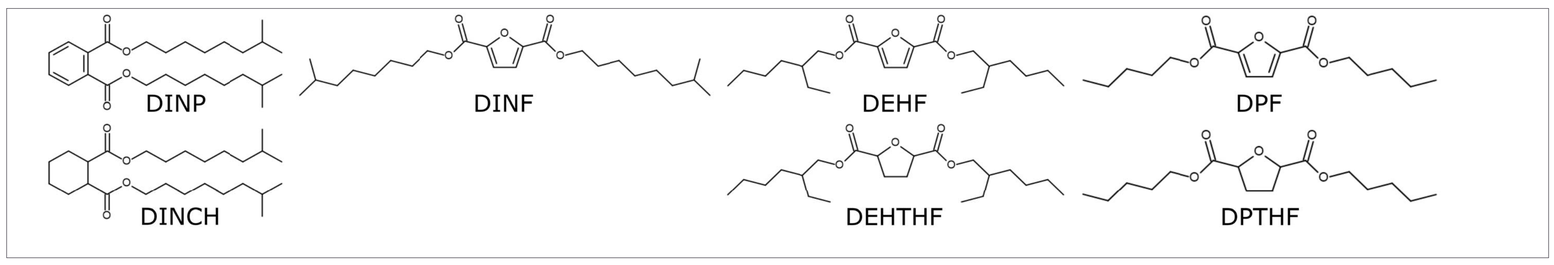

Figure 2: Selection of synthesized substances sorted by side chain length in descending order and commercial plasticizers, whose properties and applicability as plasticizers were studied (Table 1).

Table 1: Properties of FDCA-based plasticizers, plastisols and PVC films in relation to the commercial plasticizers DINP and DINCH. Film properties: amount of plasticizer 38 ± 1 %, thickness 328 ± 10 µm.

		Target	DINP	DINCH	DINF	DEHF	DEHTHF	DPF	DPTHF
Plasticizer	Thermal stability: T_{onset} (°C)	> 200	250	-	258	232	-	-	177
Plastisol	Viscosity: $\eta_{100/s,1d}$ (Pa·s)	2-5	4	3	7	7	15	48	> 170
	Solubility temperature: θ_L (°C)	-	123	136	117	111	101	89	79
	Crossover temperature: COT (°C)	< 105	86	104	82	78	69	61	-
Film	Glas transition temperature: T_g (°C)	< -20	-33	-39	-21	-18	-21	-15	-
	Tensile strength: σ_m (MPa)	-	18	11	16	15	16	9	-
	Elongation at break: ε_B (%)	> 200	280	220	265	260	210	165	-
	Thermal stability: t (min)	-	12	10	8	11	5	10	-
	Fogging: F_g (mg)	≤ 2	3	3	3	7	42	56	-
	TVOC (µg/g)	< 30	2	2	3	5	800	23	-

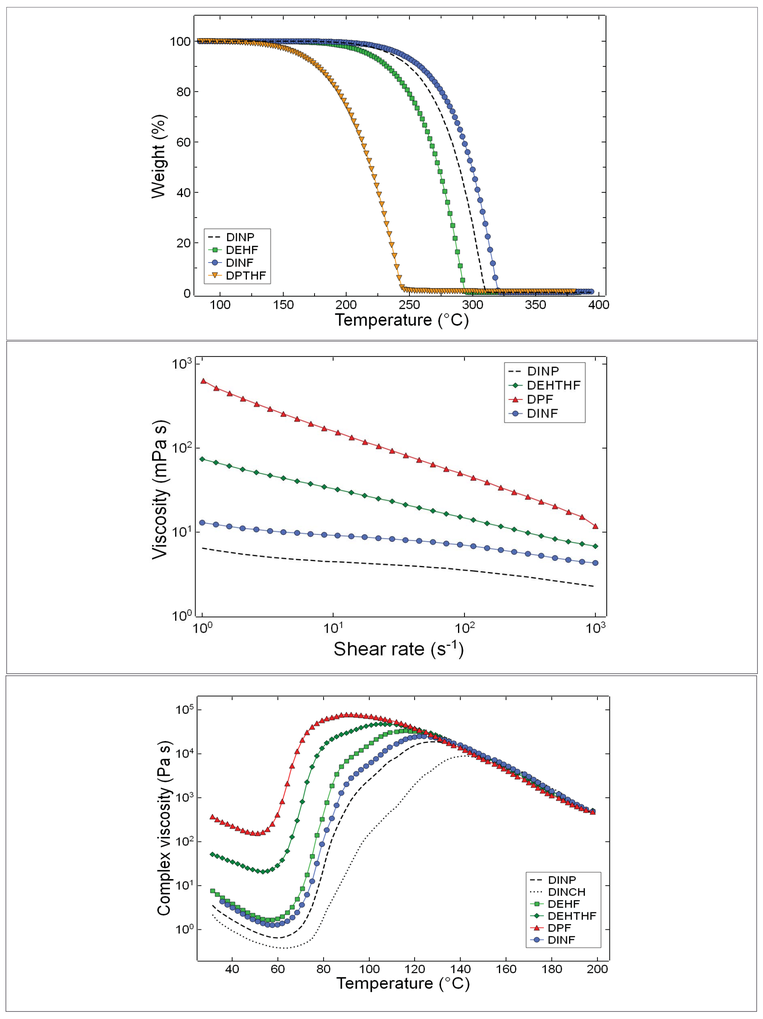

Figure 3: Top: Thermal stability of plasticizers. Middle: Plastisol viscosity depending on the shear rate indicating the processability via spread coating. Bottom: Complex viscosity of plastisols depending on the temperature showing the gelling behaviour.

CONCLUSIONS

- Highest potential for an application as plasticizer: DINF; properties comparable to DINP
- FDCA-based plasticizers superior in gelling PVC to phthalates
- High viscosity of FDCA-based plasticizers disadvantageous for spread coating
- Good mechanical properties of PVC films
- Structural similarity to phthalate plasticizers suggests beneficial properties in FDCA-based derivatives and applicability as plasticizers

OUTLOOK

- Reduction of plasticizer migration and fogging
- Influence of FDCA-derivatives with amide structures on plasticizer properties
- Investigation of processability in dryblends
- Application in coated fabrics by extrusion and roll melt coating
- Improvement of profile of properties by non-phthalate plasticizer mixtures

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CORRESPONDING AUTHOR
Maren Lehmann
Telefon+49 3731 366-210
Email: maren.lehmann@filkfreiberg.de
[1]Forschungsinstitut für Leder und Kunststoffbahnen (FILK) gGmbH
Meißner Ring 1-5 - 09599 Freiberg / Germany
www.filkfreiberg.de

PARTNER
[2]Institute of Technical and Macromolecular Chemistry (ITMC), RWTH Aachen, Germany
[3]DWI - Leibniz Institute for Interactive Materials, Aachen, Germany

ITMC RWTH, DWI Leibniz-Institut für Interaktive Materialien

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