31 (PII)

M. Lehmann[a], Z. Saleem[b], S. Fritz[a], B. Morgenstern[a]

FILK Freiberg Institute

PLANT-BASED PLASTICIZERS AND FLAME RETARDANTS FOR P-PVC

Motivation

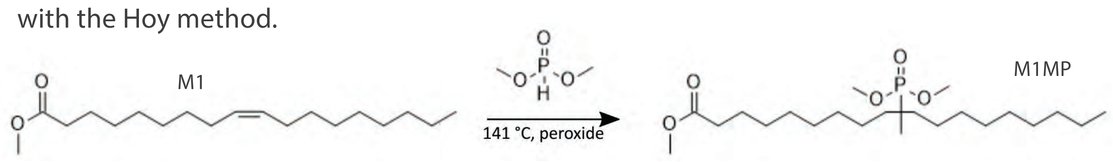
- increasing scarcity of fossil resources
- substantial public interest on 'green chemistry'
- stringent regulation regarding use of well-established general purpose phthalate plasticizers
- damaging effects of halogenated or heavy metal based flame retardants on health and environment

Aim

- increasing the thermal stability of P-PVC by use of plant oil based plasticizers
- improvement of compatibility between PVC polymer by increasing the polarity of the fatty acid ester (FAE)
- incorporation of phosphorous functionalities to provide additional thermal stability and flame retardancy

Phosphonylation of FAE

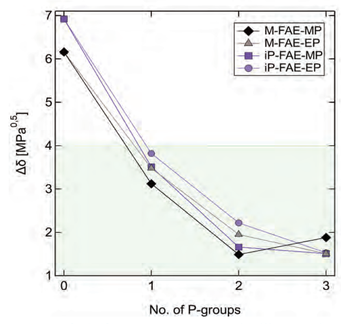
Transesterification and phosphonylation of fatty acids of high-oleic sunflower oil, rape seed oil, globe thistle oil and dragons head oil. Selection based on solubility parameter calculations with the Hoy method.



Phosphonylation of high-oleic sunflower oil methyl ester (M1) to a methyl ester of the high-oleic sunflower oil with a methylphosphonate group (M1MP) in place of the double bond.

Solubility parameters (δ) and difference in solubility parameter between plasticizer and PVC (Δδ)

	δ [MPa^{0,5}]	Δδ [MPa^{0,5}]
PVC	20.3	
DINCH	17.2	5.4
DINP	17.8	4.3
DPO	21.5	2.5
M1MP	19.0	3.1
iP1EP	18.5	3.8

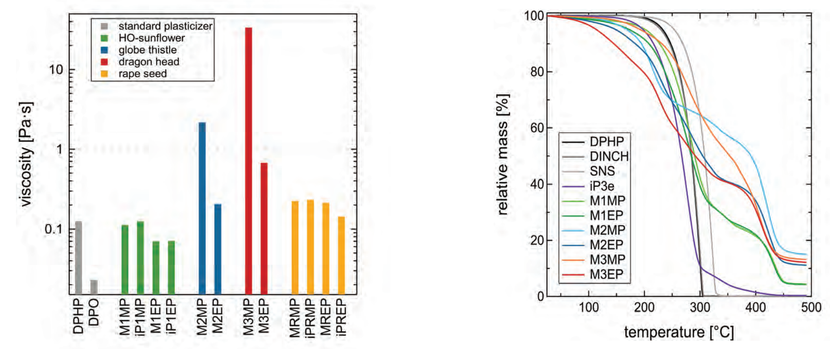


Difference in solubility parameter (Δδ) as a function of the number of phosphonate groups per FAE molecule with the green area indicating the ideal values.

- decrease in difference in solubility
- parameters (Δδ) with increasing
- number of phosphonate groups per FAE molecule
- Δδ increases with length of alkyl chains in phosphonate groups as polarity decreases

Phosphorous plasticizers

The performance potential of phosphonylated FAE (pFAE) was compared to standard plasticizers and was based on viscosity and thermal behavior (TGA).



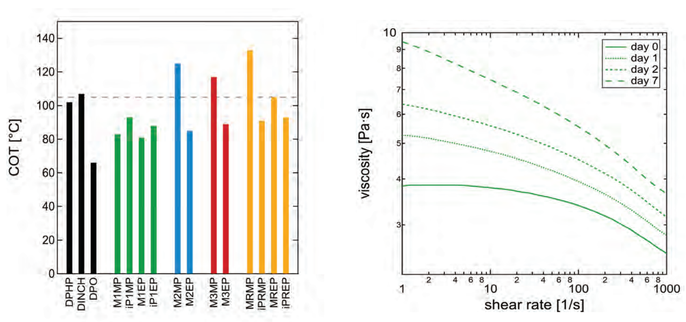
Left: Viscosity of the plasticizers depending on their composition. Right: TGA curves showing the reduction in relative mass upon increasing temperature.

- increase in viscosity with increasing No. of P-groups per FAE molecule
- FAE with methylphosphonate groups based on globe thistle and dragons head oil not processible
- multi-step decrease in mass with increasing temperature and > 4 % residual mass for pFAE due to phosphorus content
- residual mass correlates with theoretical phosphorus content based on the chemical structure

Plant Based Oils

PVC plastisols with pFAE

Plastisols with PVC (K value 70), 65 phr plasticizer and 2 phr thermostabilizer were used for the screening for gelation, solution temperature, time-dependent viscosity and thermal stability.



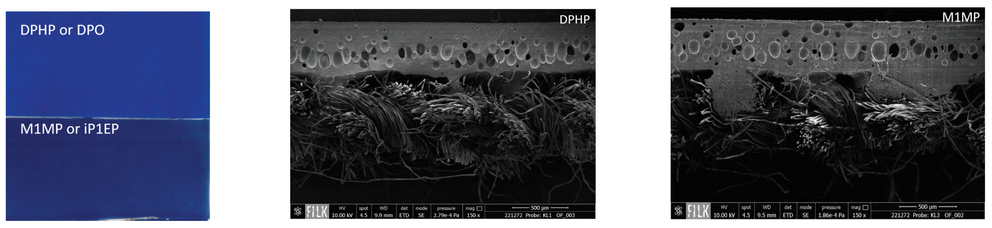
	$T_{solv.}$ [°C]	$t_{stab.}$ [h]
DPHP	133	0.25
DINCH	136	0.38
DPO	98	0.30
M1MP	112	0.97
iP1EP	119	1.21
iPREP	120	0.78

Left: Cross-over-temperatures (COT) from rheological gelation curves. Middle: Viscosity of iP1EP depending on the day on or after plastisol preparation. Right: Solution temperature ($T_{solv.}$) and stability time ($t_{stab.}$) by dehydrochlorination (similar to ISO 182-3) for selected plasticizers.

- excellent gelation behavior with cross-over-temperatures (COT) of 81-105 °C for most pFAE
- increasing viscosity of plastisol as time after preparation increased
- plastisols with HO-sunflower and rape seed oil based pFAE still processible after 2 days of ripening (viscosity < 10 Pa·s)
- solution temperature also demonstrated very good gelation behavior
- delaying dehydrochlorination of plastisols with pFAE

PVC artificial leather with pFAE

Compact PVC artificial leather consisting of top, intermediate and base layer with pFAE as plasticizer were prepared in a lab coater. Artificial leather with DPHP contained a flame retardant mix with boron and antimony.



Left: Photographs of artificial leather with blue pigment. Middle & Right: SEM images of cross sections through artificial leather with DPHP or M1MP.

- pFAE influence color and foaming of artificial leather
- self-extinguishing behavior of all samples with smaller burning rate for M1MP
- higher thermal stability for artificial leather with M1MP

Results of testing limiting oxygen index (LOI), thermal stability by dehydrochlorination (similar to ISO 182-3), horizontal burning behavior (similar to DIN 75200) and maximum heat release rates by cone-calorimetry; *- determined before reaching first measuring mark

	DPHP	DPO	M1MP
LOI [% O_2]	23.8	25.5	25.8
therm. stability [h]	0.5	0.7	1.2
burning behavior	SE/0	SE/0	SE/0
burning rate* [mm/min]	21	23	19
peak heat release rate [kW/m^2]	203.3	-	107.9

Conclusion

→ pFAE are good candidates for application as alternative plasticizers.

→ pFAE based on locally sourced plant oils displayed best plasticizer performance and good flame retardancy effects.

→ Favorable lower gelation and solution temperatures of pFAE compared to phthalate

→ plasticizers.

→ Gelation behavior improved and viscosity decreased with increasing length of alkyl chain in phosphonate group.

→ Smaller differences in solubility parameter between pFAE and PVC was not enough to increase plasticizer performance as viscosity increased significantly.

→ Flame retardancy improved by pFAE to such an extend that no additional flame retardants were necessary.

Contact
[a] Dr. Maren Lehmann
FILK Freiberg Institute gGmbH
Meißner Ring 1-5
09599 Freiberg / Germany

Partner
[b] Zuhair Saleem
Pilot Pflanzenöltechnologie Magdeburg e.V. (PPM)
Magdeburg, Germany

Acknowledgement
The research projects IGF Nr. 21183 BR and 22362 BR were and are funded by the Federal Ministry of Economic Affairs and Climate Action (BMWK) within the funding program "Industrielle Gemeinschaftsforschung (IGF)" via „Arbeitsgemeinschaft industrieller Forschungsvereinigungen e.V. (AiF)" on the basis of a decision by the German Bundestag. We would like to thank for the support granted.

Supported by:
Federal Ministry for Economic Affairs and Climate Action
on the basis of a decision by the German Bundestag

Scan me!