



Daniel Ortiz Martinz
TMD Paste PVC – SolVin SA/ Vinyls R&T

Evaluations on Alkyl Epoxy Stearate Plasticisers in Paste PVC Applications Meeting with Petrom

Brussels – June 17th, 2011

Bio-based Plasticisers for PVC



Purpose & Assessed Bio-Plasticisers

- The purpose of this work was to assess different alky epoxy stearates (soyates) plasticisers as potential alternatives for current General Purpose (GP) Phthalates;
- Three bio-base plasticisers from Petrom S.A (Brazil) were evaluated in comparison with DEHP, DINP and DIDP (see table below);
- Both transparent and foamy Paste PVC formulations were taken into consideration in our studies.

Plasticiser	Manufacturer	Country	Bio-Based Content	Feedstock	Chemical Name	MW (g/mol)
DEHP	Arkema	France	0%	crude	Di (2-ethylhexyl) phthalate	390
DINP	BASF	Germany	0%	crude	Di-isononylphthalate	418
DIDP	Exxon	WE	0%	crude	Di-isodecylphthalate	446
PLS Green® 5	Petrom SA	Brazil	100%	soybean	Amyl epoxy stearate	365
PLS Green® 8	Petrom SA	Brazil	68%	soybean	Octyl epoxy stearate	407
PLS Green® 9	Petrom SA	Brazil	66%	soybean	Nonyl epoxy stearate	421

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Experimental : Paste PVC Evaluations & Recipes

- Mixing Conditions: pastes prepared at a medium speed mixer and de-aerated before assessment. Two types of recipes:

1. Transparent formulations (flooring-type, wear layers)

Raw Material	Quantity (phr)
SolVin® 382NG	100
Plasticiser	50
Baerostab NT 306 (Ca/Zn)	2.5

- Evaluations: viscosity, paste ageing, air entrapment/ air release, thermal stability, weight loss, color, gloss and transparency

2. Foamy formulations (flooring-type, decor layers)

Raw Material	Quantity (phr)
SolVin® 367NK	100.0
Plasticiser	62
CaCO3 (15 µm)	40
Porofor ADC (50%) + DINP(50%)	6
Baerostab KK42	2.0

- Evaluations:
 - 1) Pastes => viscosity & paste ageing
 - 2) Foams => density, expansion rates, cell quality and colour (Yellow index)

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Experimental : Recipes & Renewable Content

- When switching from crude-based plasticisers to bio-based ones, the total content of renewable materials in the formulations increases:

1. Transparent formulations

Raw Material	Quantity (phr)
SolVin® 382NG	100
Plasticiser	50
Baerostab NT 306 (Ca/Zn)	2.5

Original¹ Renewable Materials Content (%) = 0%;



Renewable² Materials Content with Bio-based Plasticisers(%) = 22 to 33%

2. Foamy formulations (flooring-type, decor layers)

Raw Material	Quantity (phr)
SolVin® 367NK	100.0
Plasticiser	62
CaCO3 (15 µm)	40
Porofor ADC (50%) + DINP(50%)	6
Baerostab KK42	2.0

Original¹ Renewable Materials Content (%) = 0%;



Renewable² Materials Content with Bio-based Plasticisers(%) = 20 to 30%

¹ If we consider chlorine inexhaustible, the renewable content will be 27% and 38%

² With Bio-Based PVC the renewable content would increase to 50-60%

Bio-based Plasticisers for PVC



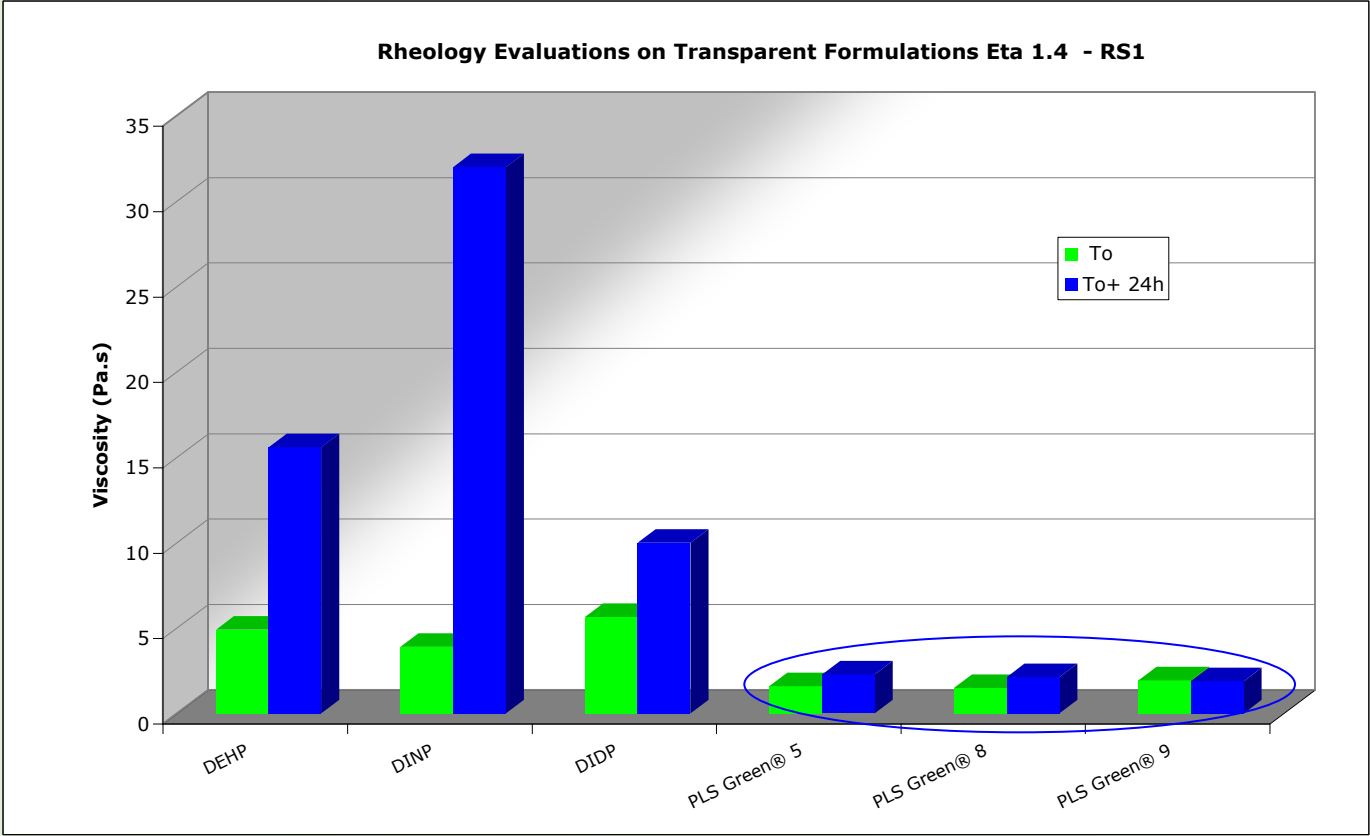
Experimental - Part 1

Transparent Layers Evaluations

Bio-based Plasticisers for PVC



Transparent Paste PVC: Rheology & Paste Ageing

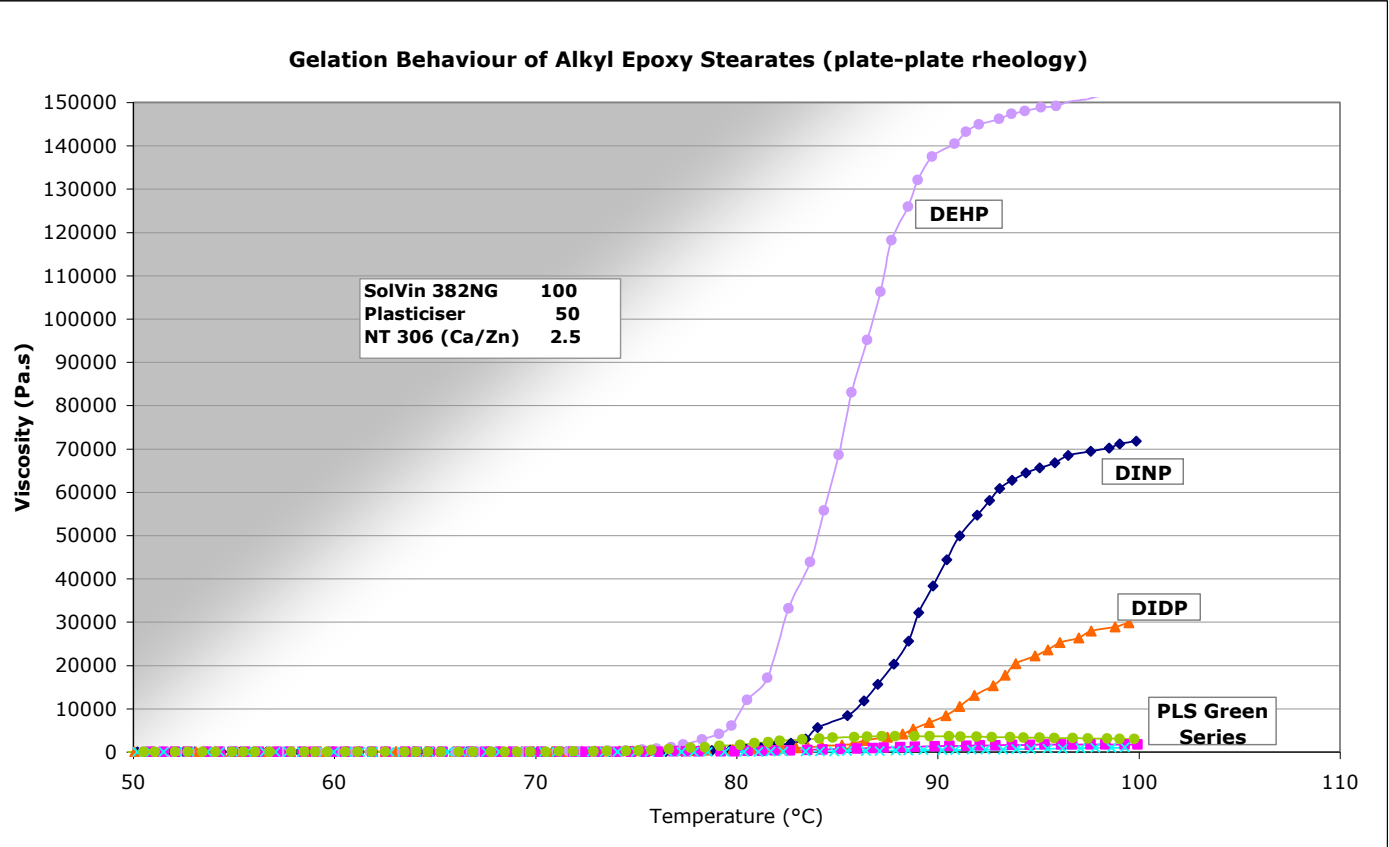


- Lowest viscosities were obtained for ESBO-based plasticisers (alkyl epoxy estearates). Paste ageing of these three bio-based materials was excellent. All pastes are newtonian or slightly pseudoplastic (phthalates, after 24h)

Bio-based Plasticisers for PVC



Transparent Paste PVC: Gelation Behaviour

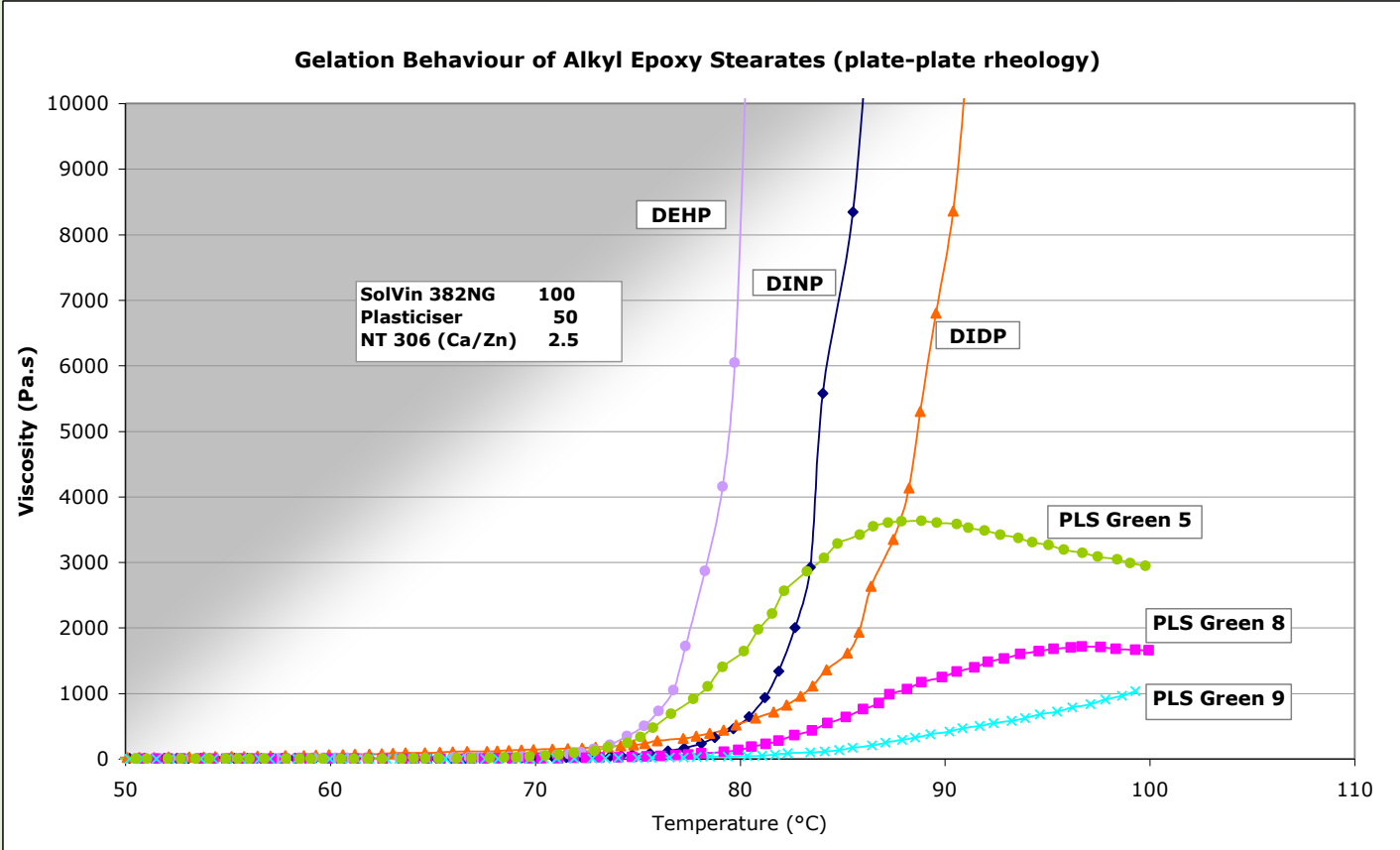


- GP Phthalates gelate faster than alkyl epoxy stearates. Highest viscosities were obtained for GP phthalates during gelation

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Transparent Paste PVC: Gelation Behaviour (zoom)



- Gelation speed: DEHP > DINP > DINP >> PLS Green® 5 > PLS Green® 8 > PLS Green® 9. Gelation is a faster for lower MWs within homologous series

Bio-based Plasticisers for PVC



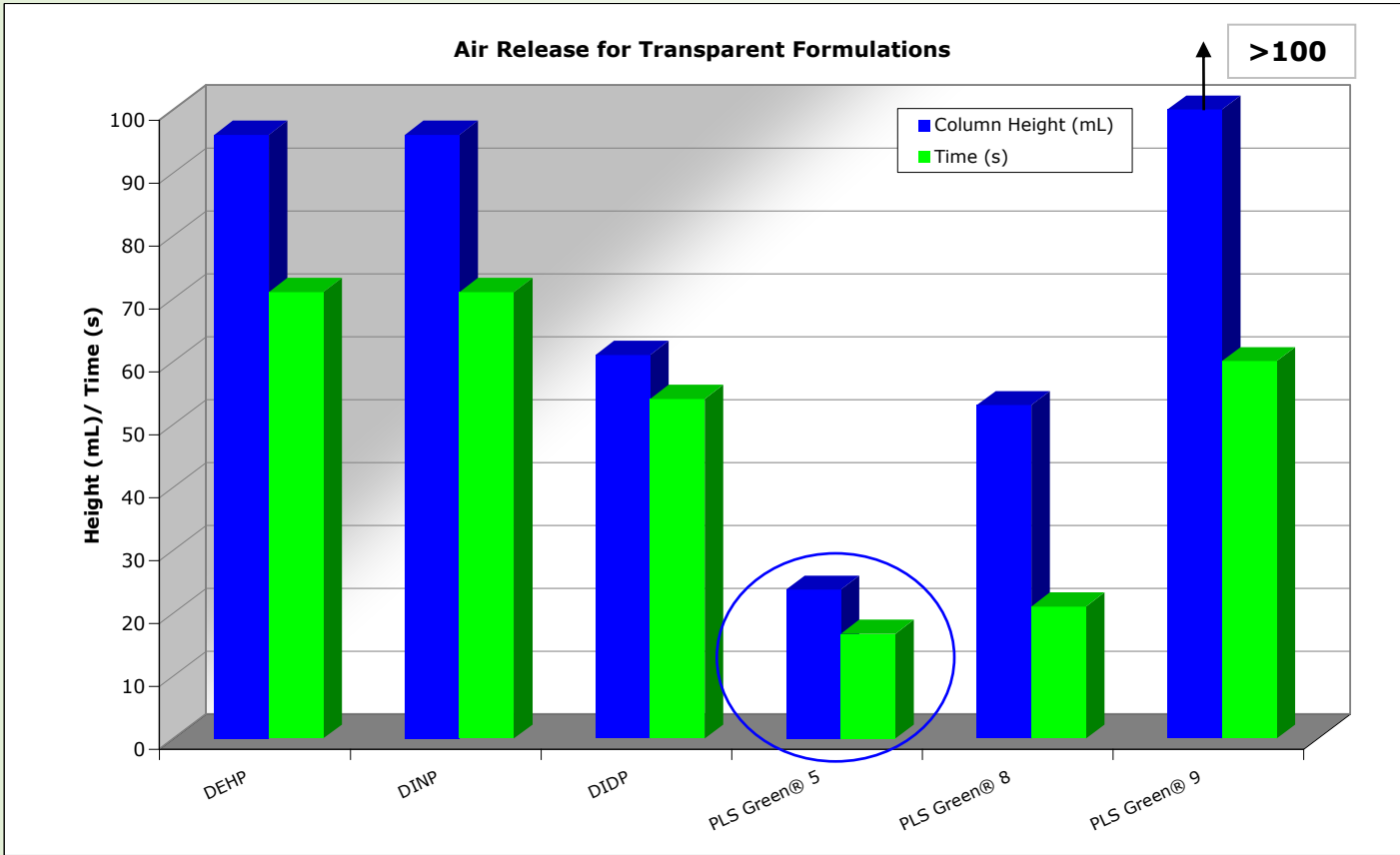
Transparent Paste PVC: Air Release & Air Entrapment

- Air release & air entrapment of pastes were assessed according to internal methods;
- Air release is expressed in terms of the maximum height of plastisol column and the time to collapse this column (break of surface tension)
- For air entrapment evaluations, after a 5 minutes de-aeration, pastes were gelled in a Werner Mathis oven for 2 min at 200° C (thickness: 0.3mm).
- Pastes were then re-stirred during 1 and 5 minutes. The re-stirred plastisols were again gelled at the same conditions as before. Photos were taken (the bubbles are the black spots) and scores were visually attributed afterwards.

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Transparent Paste PVC: Air Release



■ The lower the values, the better => PLS Green 5 is the best in class, followed by PLS Green 8.

Bio-based Plasticisers for PVC



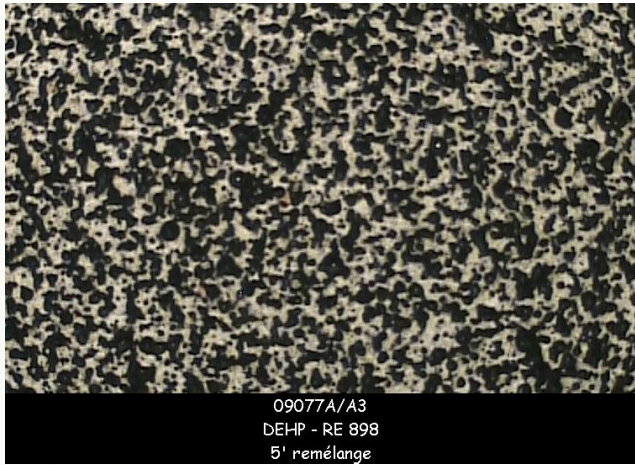
Transparent Paste PVC: Air Release & Air Entrapment

after air removal

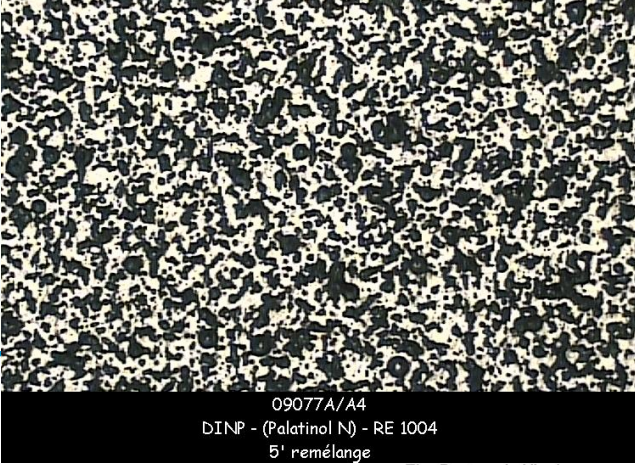
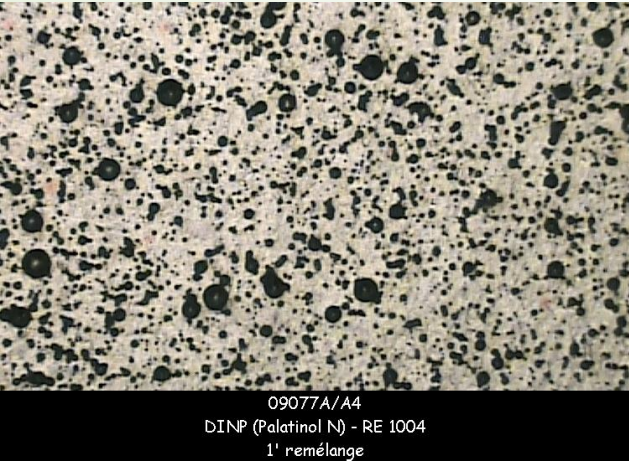
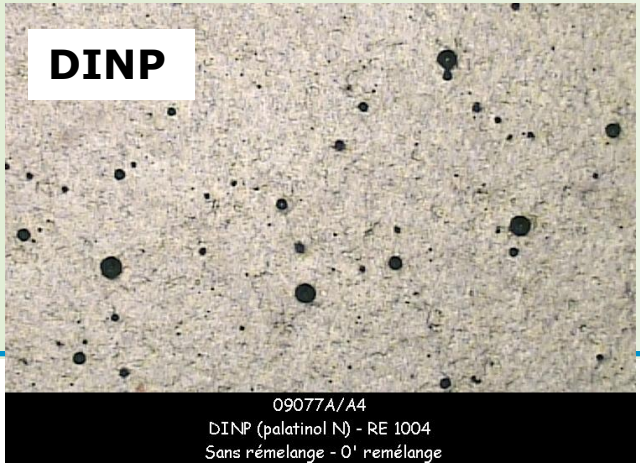
after 1 min of re-stirring

after 5 min of re-stirring

DEHP



DINP



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Transparent Paste PVC: Air Release & Air Entrapment

after air removal

after 1 min of re-stirring

after 5 min of re-stirring

PLS Green 5

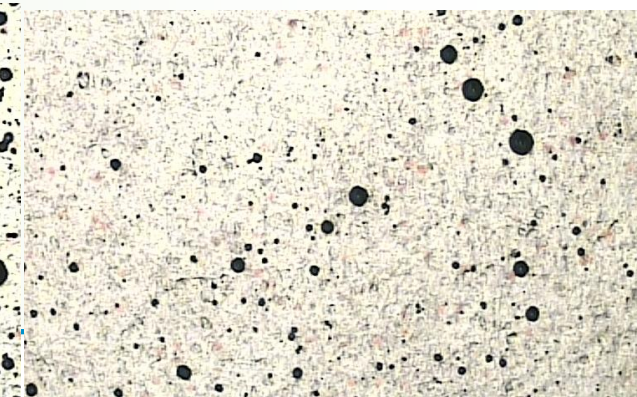
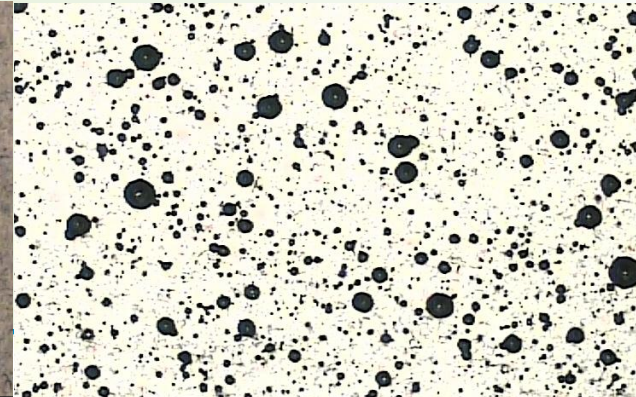
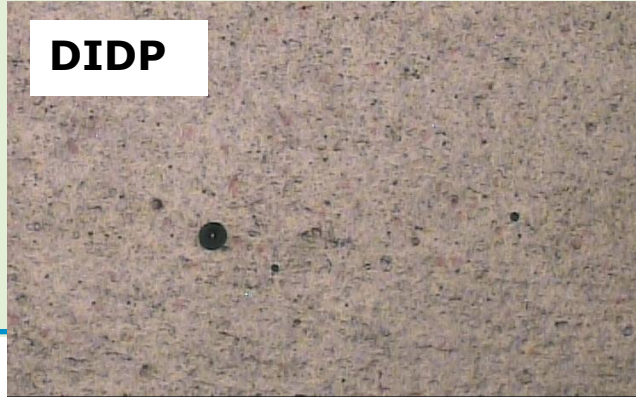


10097 A/A4
PLS Green 5 - 2010-11-17/07
sans remélange

10097 A/A4
PLS Green 5 - 2010-11-17/07
1' de remélange

10097 A/A4
PLS Green 5 - 2010-11-17/07
5' de remélange

DIDP



10007A/1
DIDP - RE 812
Sans remélange

10007A/1
DIDP - RE 812
1' de remélange

10007A/1
DIDP - RE 812
5' de remélange

Bio-based Plasticisers for PVC



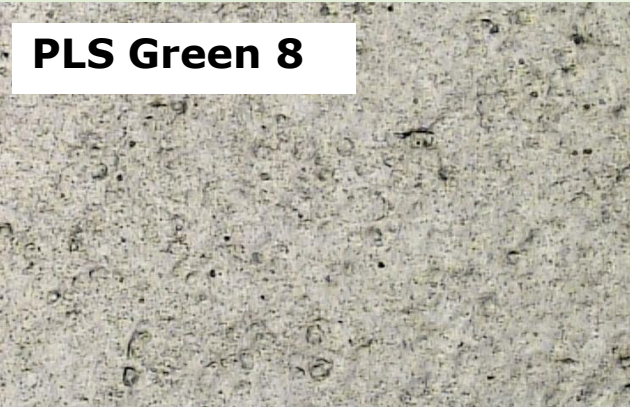
Transparent Paste PVC: Air Release & Air Entrapment

after air removal

after 1 min of re-stirring

after 5 min of re-stirring

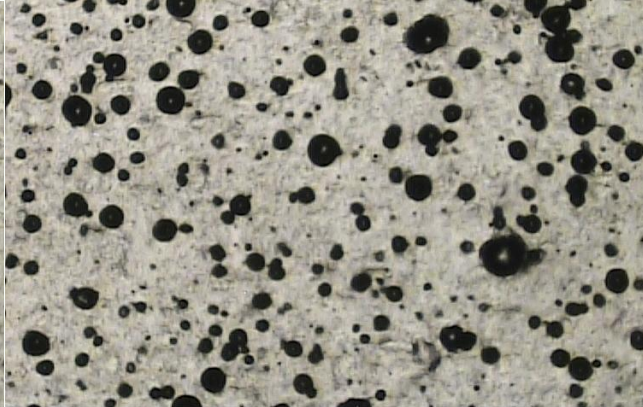
PLS Green 8



10097 A/A5
PLS Green 8 - 2010-11-17/08
sans remélange

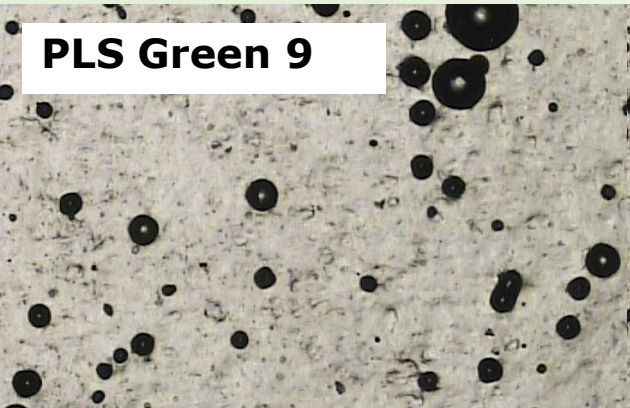


10097 A/A5
PLS Green 8 - 2010-11-17/08
1' de remélange

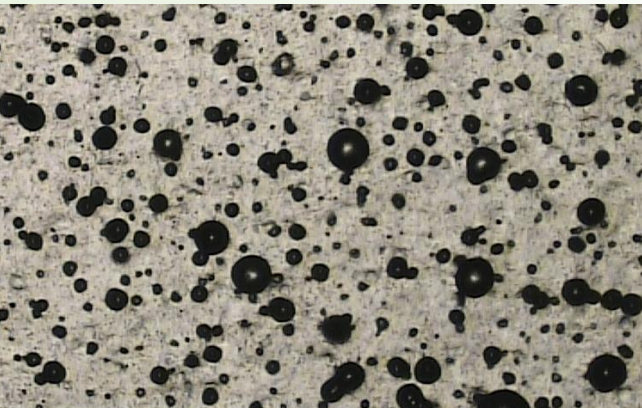


10097 A/A5
PLS Green 8 - 2010-11-17/08
5' de remélange

PLS Green 9



10097 A/A6
PLS Green 9 - 2010-11-17/09
sans remélange



10097 A/A6
PLS Green 9 - 2010-11-17/09
1' de remélange



10097 A/A6
PLS Green 9 - 2010-11-17/09
5' de remélange

Bio-based Plasticisers for PVC



Transparent Paste PVC: Thermal Stability

- Thermal stability of pastes was assessed regarding DHC (dehydrochlorination, 180° C) and Metrastat (190° C).

Plasticiser	DHC ¹ (min)	Metrastat (min)
DEHP	26	10
DINP	28	14
DIDP	25	13
PLS Green® 5	NM ²	NM ³
PLS Green® 8	159	NM ³
PLS Green® 9	142	NM ³

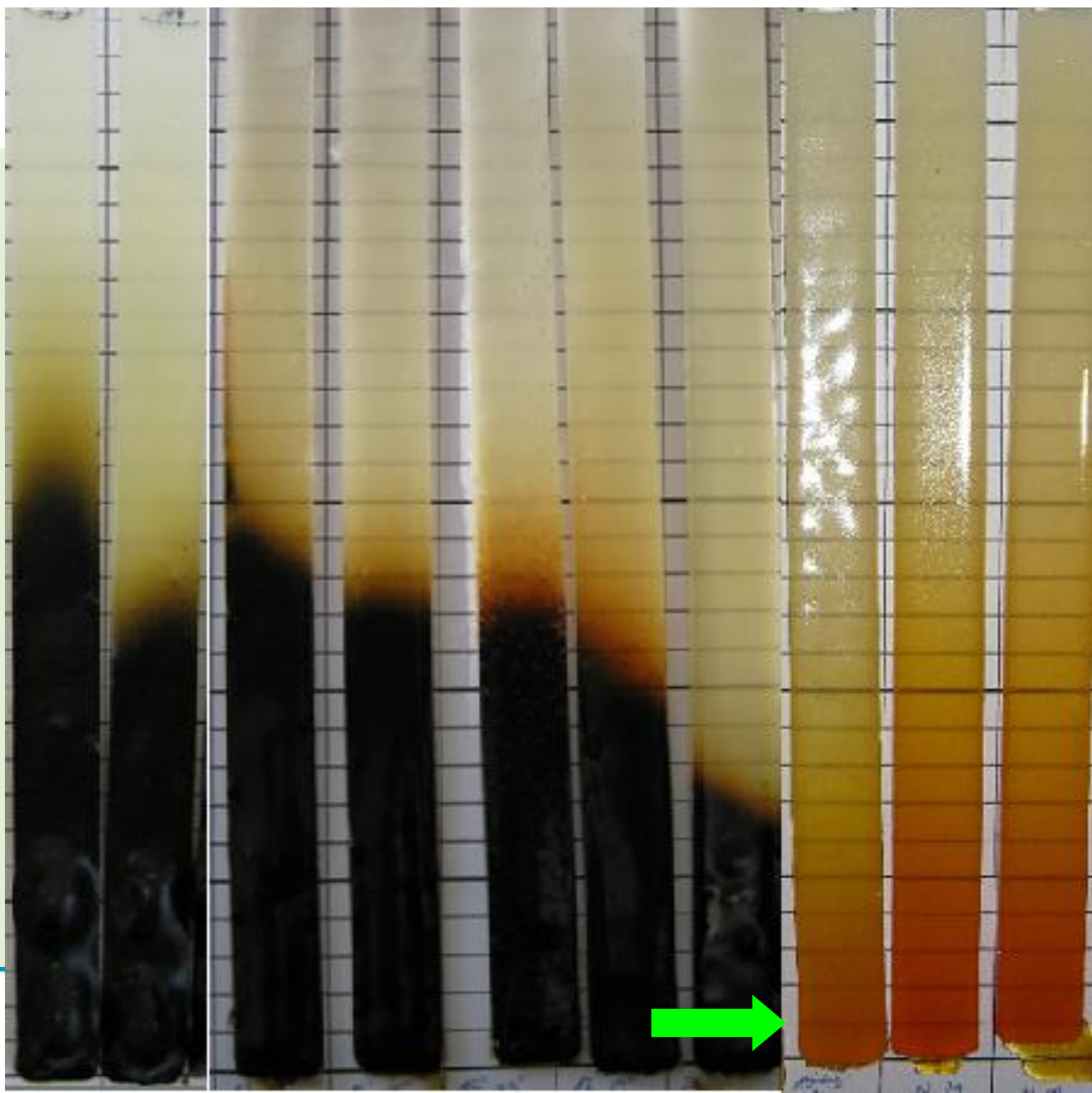
- All ESBO-based materials are outstanding.

¹ Time to reach a conductivity of 50 mS/cm

² Non-measurable

³ Non-measurable: test stopped after 3 hours

DEHP DINP DIDP DOTP 2088 SNS ID37 PLS 5 PLS8 PLS 9



astat)

PLS Green Series

Bio-based Plasticisers for PVC



Transparent Paste PVC: Colour, Gloss & Transparency of Films

Conditions: 0.7 mm, 190°C, 2 min

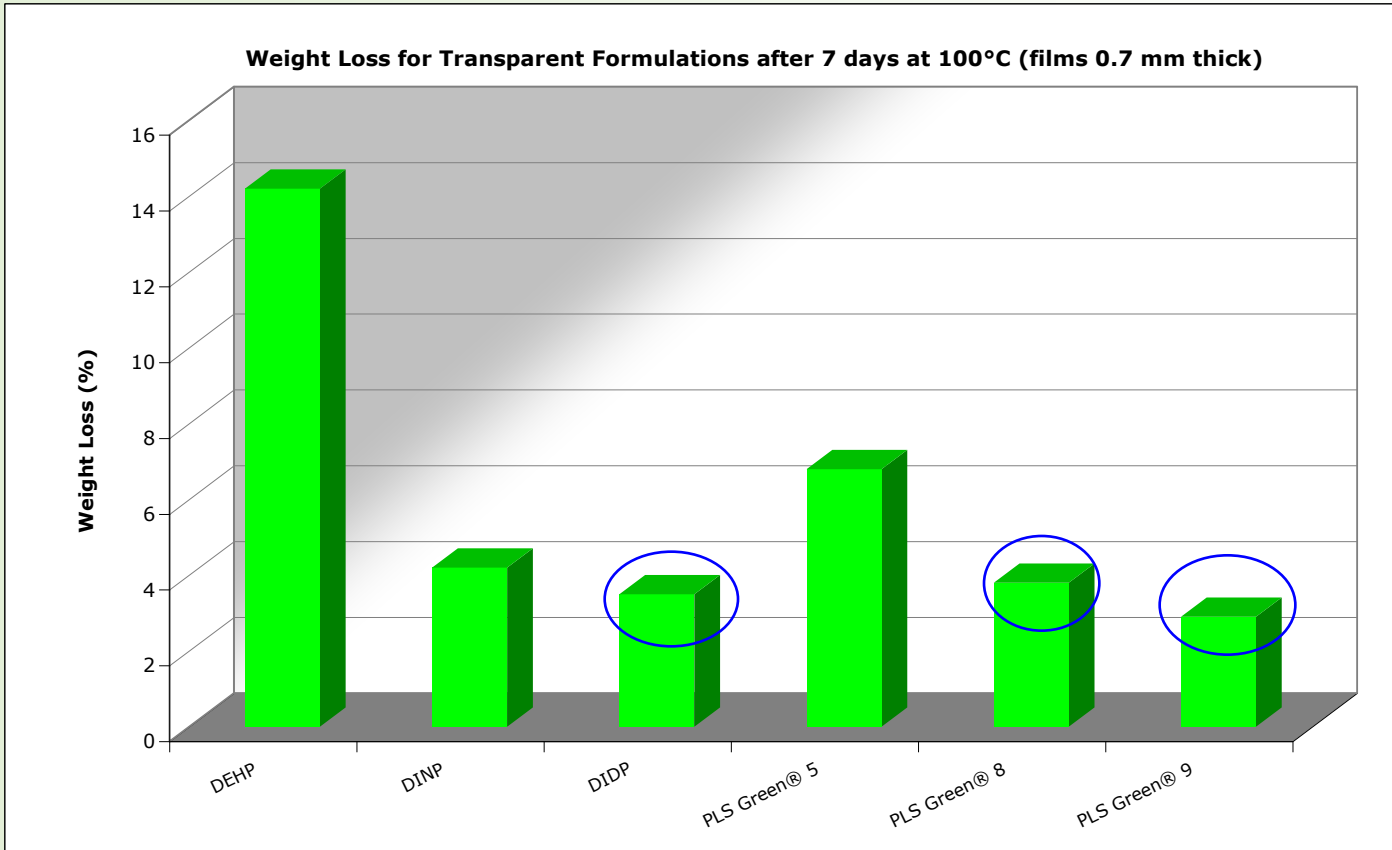
Plasticiser	Yellow Index	Gloss	Transparency
DEHP	8,1	25,6	78,9
DINP	7,4	27,7	86,1
DIDP	8,5	22,4	80,4
PLS Green® 5	12	24,8	72,9
PLS Green® 8	10,7	30,1	72,6
PLS Green® 9	11,9	32,8	69

- ESBO-based materials (PLS Green series) are more yellowish and less transparent than GP plasticisers;
- PLS 8 and PLS9 are glossier than GP phthalates

Bio-based Plasticisers for PVC



Transparent Paste PVC: Weight Loss of Films

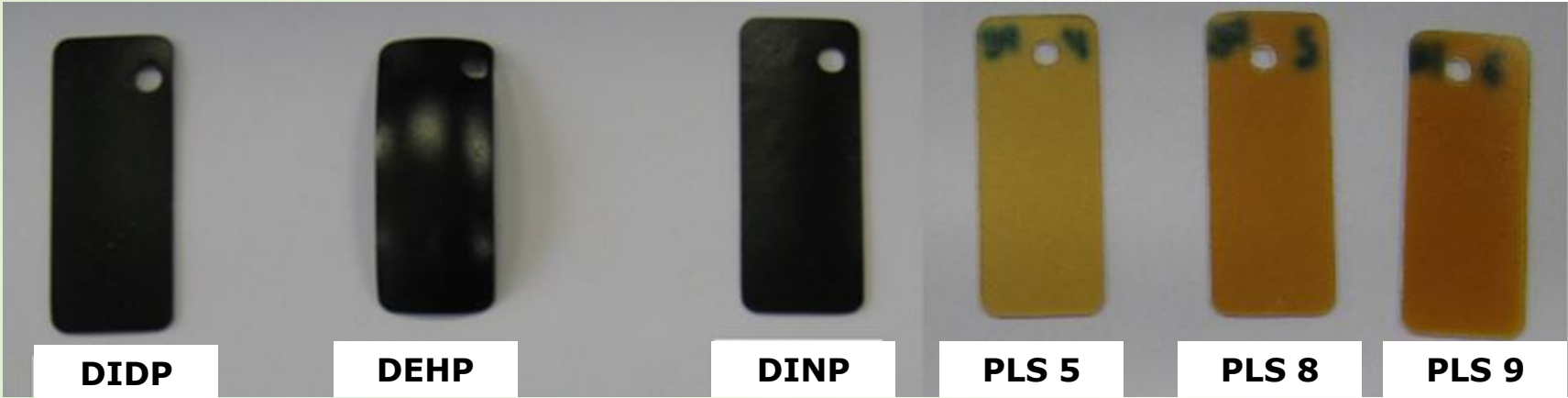


- Best results were obtained for PLS Green® 9 (~DIDP) and PLS Green® 8 (~DINP)

Bio-based Plasticisers for PVC



Transparent Paste PVC: Weight Loss of Films



- All ESBO-based plasticisers presented good colour retention after 7 days: other materials were carbonised;
- Thermal Stability: PLS 5 > PLS8 > PLS9 (the higher the epoxy concentration, the higher the TS)

100°C – 7 days
Films 0.7 mm thick

Bio-based Plasticisers for PVC



Transparent Paste PVC: Summary of Results

really poor	poor	worse	slightly worse	same	slightly better	better	excellent	outstanding
---	--	-	0/-	0	0/+	+	++	+++

Plasticiser	Rheology	P. ageing	Gelation	Air Release	T. Stability	Colour	Transp	Gloss	W Loss	Score
DEHP	0/-	+	+	0	0	0	0/-	0	--	-1
DINP	0	0	0	0	0	0	0	0	0	0
DIDP	0/-	+	-	0/+	0	0	0/-	0/-	+	0
PLS Green® 5	+	++	--	++	+++	-	-	0	-	3
PLS Green® 8	+	++	--	+	++	-	-	0/+	0	2,5
PLS Green® 9	+	++	--	-	++	-	-	0/+	+	1,5

- All the three alkyl epoxy stearates obtained high score and can be considered (from the technical point-of-view) promising alternatives to GP plasticisers in simple transparent formulations;

Bio-based Plasticisers for PVC



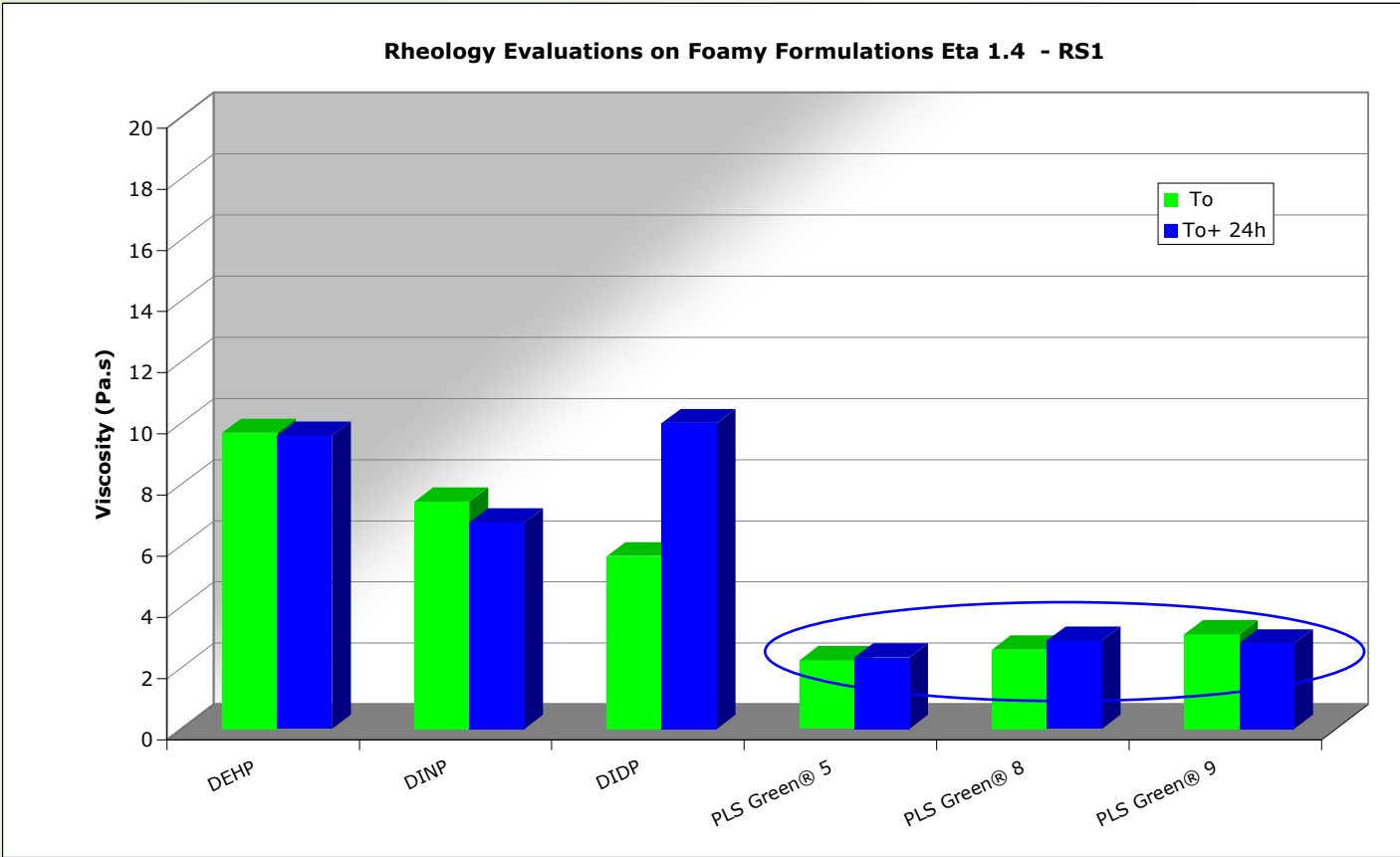
Experimental - Part 2

Foamy Layers Evaluations

Bio-based Plasticisers for PVC



Foamy Paste PVC: Viscosity & Paste Ageing



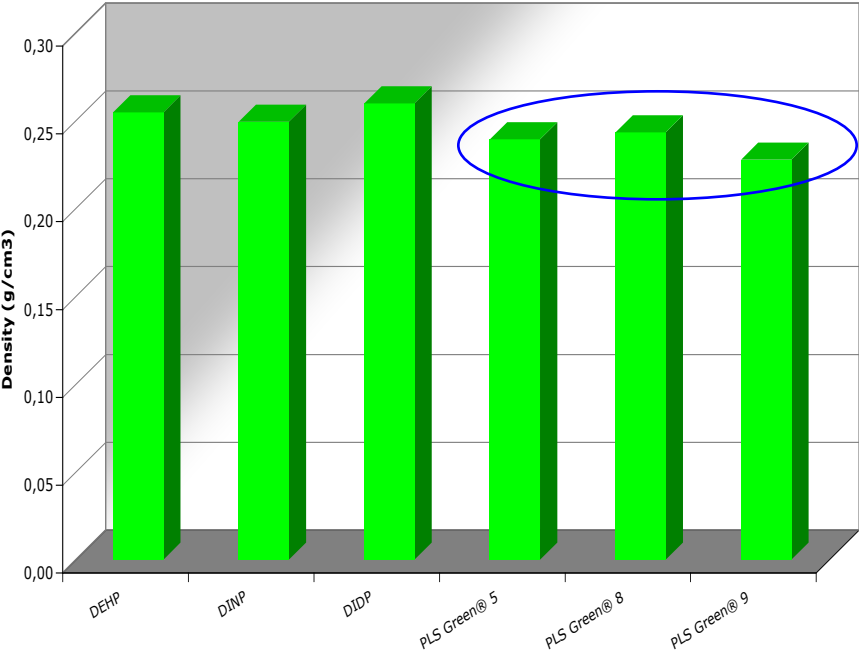
- Lowest viscosities were obtained for ESBO-based plasticisers (PLS5, PLS8 and PLS9).

Bio-based Plasticisers for PVC

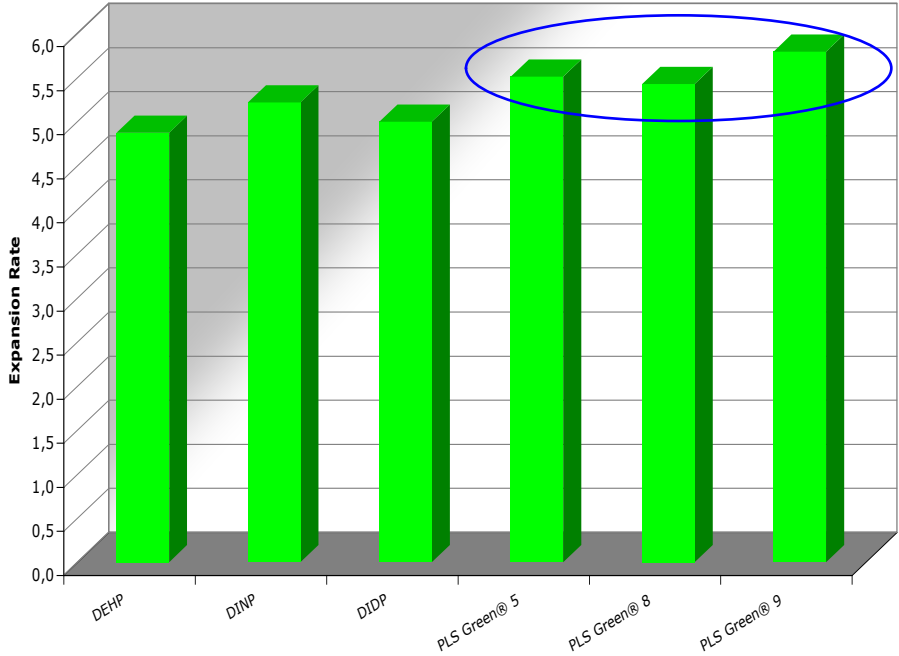


Foamy Paste PVC: Density & Expansion Ratio

Foam Densities at 200°C (2 minutes, 0.35 mm thickness)



Expansion Rates at 200°C (2 minutes, 0.35 mm thickness)



- Generally speaking, bio-based plasticisers (PLS Green® series) expand faster than GP plasticisers and therefore present slightly lower densities

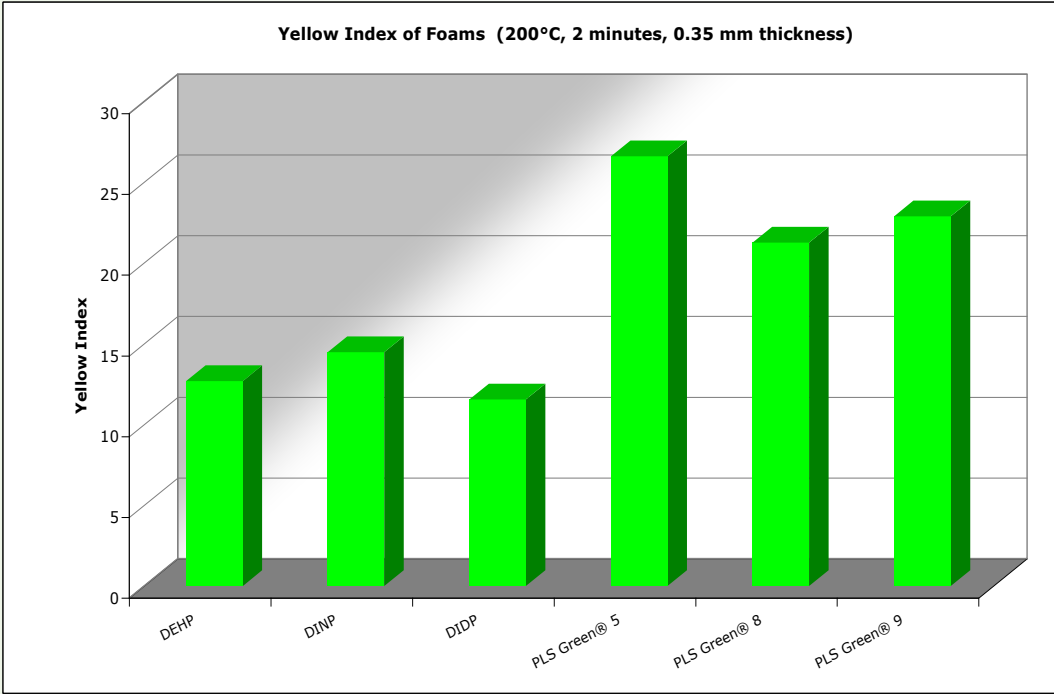
Bio-based Plasticisers for PVC



Foamy Paste PVC: Foam Quality & Colour

Plasticiser	Cell Quality (visual)
DEHP	very good
DINP	very good
DIDP	very good
PLS Green® 5	very good
PLS Green® 8	medium
PLS Green® 9	medium

- Cell qualities of PLS Green 5 are comparable to those of GP plasticisers



- All the three bio-based materials are more yellowish than GP plasticisers.

Bio-based Plasticisers for PVC



Foamy Paste PVC: Summary of Results

really poor	poor	worse	slightly worse	same	slightly better	better	excellent	outstanding
---	--	-	0/-	0	0/+	+	++	+++

Plasticiser	Rheology	P. ageing	Color	Density	Exp Rate	Cell Quality	Score
DEHP	0/-	0	0/+	0	-	0	-1
DINP	0	0	0	0	0	0	0
DIDP	0/+	-	0/+	0/-	0/-	0	-1
PLS Green® 5	+	0	-	0/+	+	0	1,5
PLS Green® 8	+	0	-	0/+	+	-	0,5
PLS Green® 9	+	0	-	+	++	-	2

- All the three alkyl epoxy stearates can be considered (from the technical point-of-view) promising alternatives to GP plasticisers in foamy formulations.

Bio-based Plasticisers for PVC



Paste PVC Formulations: Overall Performance

Plasticiser	Score Transparent Layers	Score Foamy Layers	Total Score
DEHP	-1	-1	-2
DINP	0	0	0
DIDP	0	-1	-1
PLS Green® 5	3	1,5	4,5
PLS Green® 8	2,5	0,5	3
PLS Green® 9	1,5	2	3,5

- **PLS Green® 5**, **PLS Green® 8** and **PLS Green® 9** are promising alternatives to GP plasticisers in paste PVC formulations



**Thanks for your
attention!**

Daniel Ortiz Martinz
daniel.martinz@solvay.com

Brussels – June 17th, 2011