Evaluation of Processing Performance of Bio-Based Plasticisers in Paste PVC Applications

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Bio-based Plasticisers for PVC



General Context – Plasticisers & Phthalates

- Plasticisers are additives used to increase flexibility of PVC by shielding polymer chains one from another, allowing higher mobility of molecules;
- General purpose (GP) phthalates represent 85% of the global plasticiser consumption (6.0 MTon/year). Among the GP phthalates, DEHP, DINP and DIDP account for more than 83% of the world demand (DEHP stands for 50%);
- In Western Europe the plasticiser market was 963 Kton in 2007, 92% of which phthalates, mostly high molecular weight ones (DINP and DIDP represent 65%);
- Low molecular weight phthalates like DEHP, BBP, DIHP and DIBP are being subject of restrictions by the EU legislation (REACH);
- Phthalates are **100%** manufactured from **fossil fuels** (crude), what poses some issues in terms of carbon footprint and long-term sustainability;

Bio-based Plasticisers for PVC



General Context – Plasticisers & Economics

- In Western Europe flexible vinyl is roughly a **1.1 Bi€/year** (c.a. 1.3 MTon/ year) business, divided into E-PVC (400 Mi€) and S-PVC (700 Mi€);
- **Paste PVC** markets are highly dependent of plasticisers and cannot exist without these additives: almost **100%** of E-PVC applications **require plasticiser blending**;
- In order to assure the long-term sustainability of these markets, bio-based raw materials **must be** taken into consideration;
- Bio-based plasticisers have grown in importance in the past few years as a result of increasing challenges due to climate change and sustainability issues;
- The most usual raw materials for these new plasticisers are the oils extracted from castor plant, soybean, palm, rapeseed, sunflower, linseed. Starch (corn, potatoes and wheat) became an increasing option as the alcohol source, especially in Europe.

Bio-based Plasticisers for PVC



General Context – Plasticisers & Economics

- A few years ago most of these plasticisers were able to replace only partially GP phthalates given the limited compatibility with PVC;
- Chemical functionalisations like acetylation, transesterification with different alcohols and new building blocks (levulinic ketals & isosorbides) led to much higher affinity and to molecules that can improve fast fusing, provide high thermal & UV stability and assure increased permanence;
- Replacing a GP plasticiser, however, is not an easy task. Aspects like **economics** (price and availability), **performance** (processability, long term compatibility and others) and **toxicology** have to be taken into consideration;
- Some of the world's largest producers generally have plant capacities that do not exceed **10 Kton/year**;
- Moreover, in some cases prices are closer to specialties than to GP plasticisers and not all the molecules have gone through extensive toxicological assessments;
- This situation, however, might experience some changes in the coming years…

Bio-based Plasticisers for PVC



Some Bio-Based Plasticisers Producers - Worldwide

Company	Continent	Country	Capacity[1] (ton/y)	Raw Materials	Base Chemistry
Segetis/ Polyone	N. America	USA	100[2]	Agricultural Feedstocks/ Soybean	L-Ketals (esters of glycerol and levulinic acid)/ Alkyl epoxy soyate
Dow Wire & Cable	N. America (?)	USA (?)	-	-	-
Danisco	Europe	Denmark	5000[3]	Castor Oil	Acetylated castor oil
Roquette Frères	Europe	France	5000[4]	Starch (maize, corn, wheat, potato , pea)	Esters from isosorbides and fatty acids
Bio Amber	Europe	France	3500[5]	Cereals (wheat)	Esters from succinates
Nexoleum	S. America	Brazil	1000	Mainly Soybean	ESBO[6] (methyl epoxy soyate)
Resypar	S. America	Brazil	6000	Mainly Soybean	ESBO & Alkyl epoxy soyates
Petrom	S. America	Brazil	6000	Soybean	ESBO & Alkyl epoxy soyates
BBC	S. America	Brazil	18000	Soybean	ESBO
Imbra	S. America	Brazil	4000	Soybean	ESBO
SGS Polimeros	S. America	Brazil	18000[7]	Soybean	ESBO and alkyl epoxy soyates
Emerys Oleochemicals	S. America	Brazil	3000	Soybean (mainly) and palm	ESBO
Varteco	S. America	Argentina	36000	Soybean	ESBO
Emerys Oleochemicals	Asia	Malaysia	300000[8]	Palm	Palm oil esters
Jayant Agro-Organics	Asia	India	8000[9]	Castor Oil	Sebacates
Biotor	Asia	India	8000[9]	Castor Oil	Sebacates
Indo-Nippon	Asia	India	-	Castor Oil	Sebacates, citrates and phthalates

Obs.: [1]Declared capacities; [2]Only Segetis; [3] To be doubled; [4]To be achieved in 2012; [5]In terms of succinic acid capacity; [6]ESBO stands for epoxidised soybean oil; [7] Other products included; [8]All included (plasticisers and other additives). It will be doubled by 2015; [9]In terms of sebacid acid capacity

Bio-based Plasticisers for PVC



Purpose & Assessed Bio-Plasticisers

- The purpose of this work is to assess different bio-based plasticisers as potential alternatives for current GP plasticisers;
- Seven[1] renewable plasticisers commercially available (some of them REACH registered) from **three different continents** (Americas, Europe and Asia) were evaluated in comparison with DEHP, DINP and DIDP;
- 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)	REACH Status
DEHP	Arkema	France	0%	crude	Di (2-ethylhexyl) phthalate	390	Regist.
DINP	BASF	Germany	0%	crude	Di-isononylphthalate	418	Regist.
DIDP	Exxon	WE	0%	crude	Di-isodecylphthalate	446	Regist.
Soft-N-Safe®	Danisco	Denmark	80%	castor oil	Acelylated castor oil	505	Regist.
Polysorb® ID 37	Roquette Frères	France	**100%**	starch/ vegetal oils	Diesters from isosorbide and fatty acids	414	Regist.
Kalflex® 14A	Varteco SA	Argentina	**98%**	soybean	ESBO	974	Regist.
Nexo E01	Nexoleum	Brazil	**95%**	soybean	Methyl epoxy soyate	327[2]	Regist.
Resiflex® K50	Resypar	Brazil	**100%**	soybean	Amyl epoxy soyate	382	Not Reg
PLS Green® 9	Petrom	Brazil	**66%**	soybean	Nonyl epoxy soyate	421	Ongoing
DCS	Jayant Agro-Organics	India	**100%**	castor oil	Di-caprylsebacate	426	No info

[1] Actually we studied 20 bio-based plasticisers, but not all of them are presented for confidentiality reasons (Segetis & Bio Amber); [2]Informed by producer

Bio-based Plasticisers for PVC



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)

Bio-based Plasticisers for PVC



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

Original[1] Renewable Materials Content (%) = 0%;

Renewable[2] Materials Content with Bio-based Plasticisers(%) = 33% (max)

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

Original[1] Renewable Materials Content (%) = 0%;

Renewable[2] Materials Content with Bio-based Plasticisers(%) = 30% (max)

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[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%

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Bio-based Plasticisers for PVC



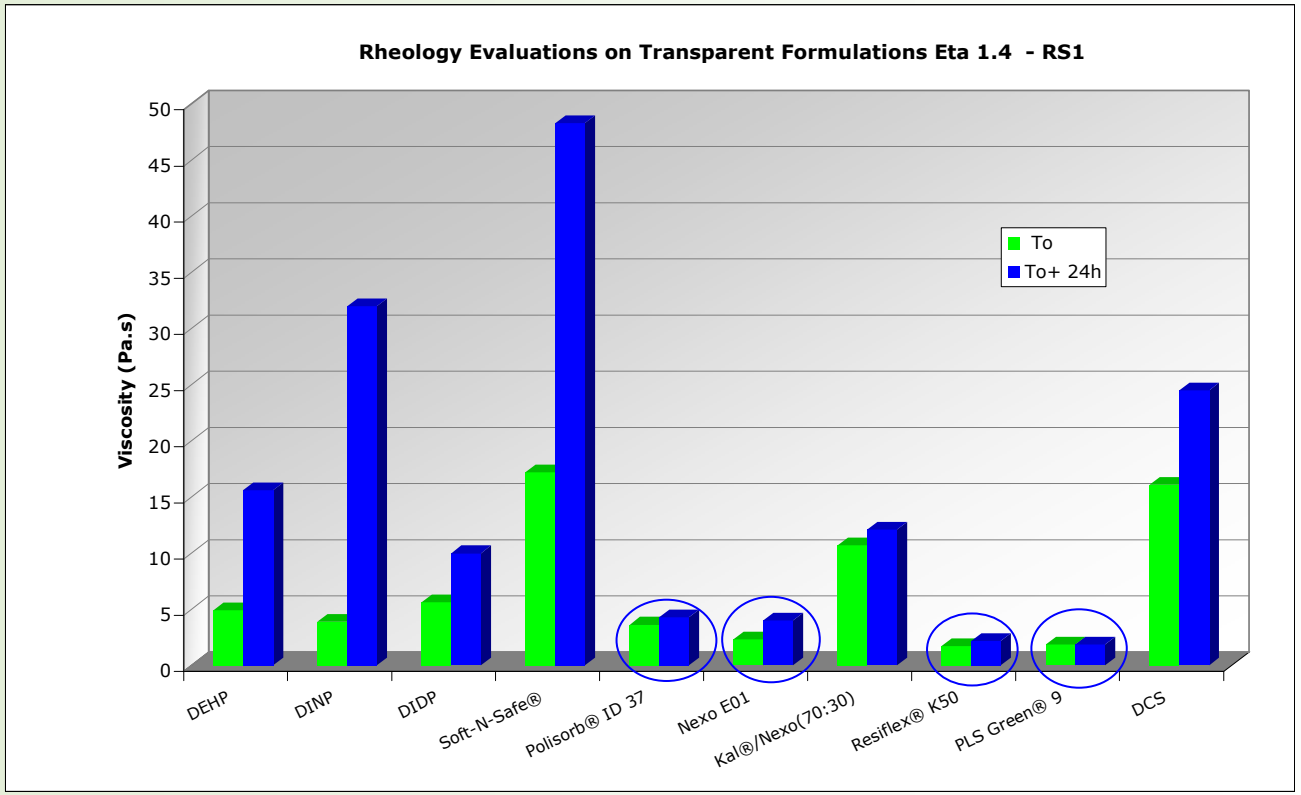
Experimental - Part 1

Transparent Layers Evaluations

Bio-based Plasticisers for PVC



Transparent Paste PVC: Rheology & Paste Ageing



- Lowest viscosities were obtained for ESBO-based plasticisers like Nexo® E01, Resiflex® K50 and PLS Green® 9. Polysorb® ID 37 also showed comparable performance with regards to DINP. Paste ageing of these four bio-based materials was excellent.

Bio-based Plasticisers for PVC



Transparent Paste PVC: Air Release & Air Entrapment

- For air release / 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.

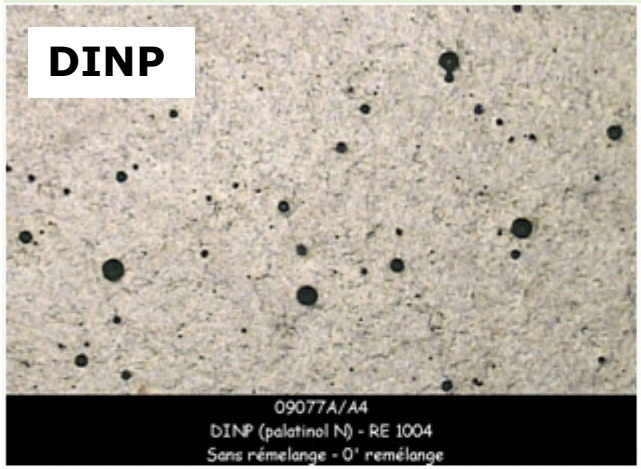
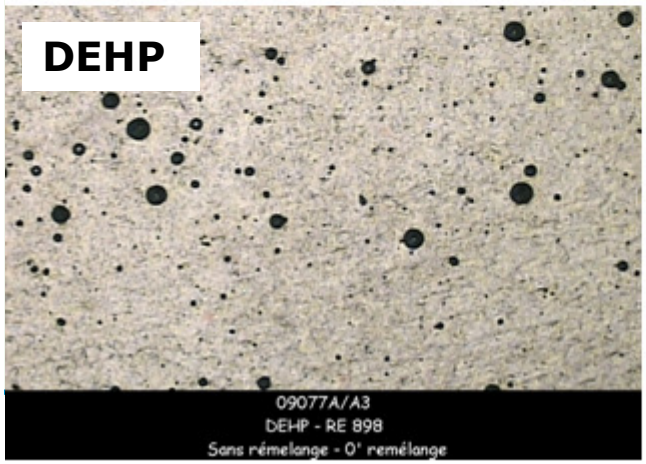
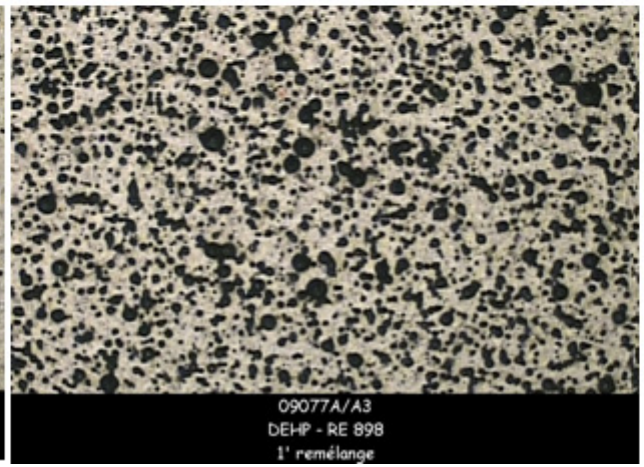
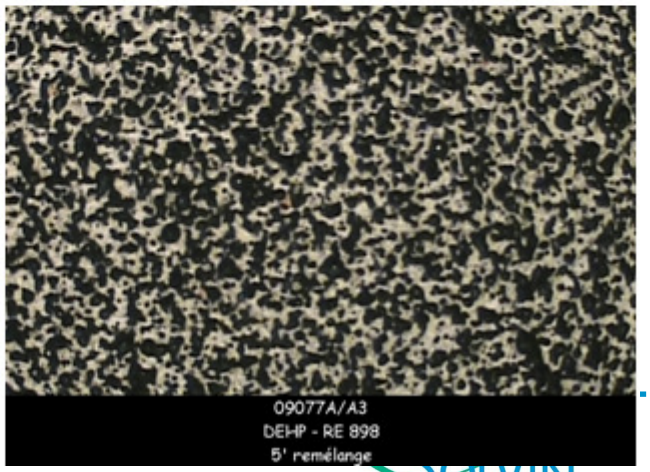
Plasticiser	After air removal	After re-stirring (1 min)	After re-stirring (5min)
DEHP	1	4	5
DINP	1	4	5
DIDP	1	3	3
Soft-N-Safe®	0.5	5	5
Polisorb® ID 37	0	3	3
Nexo E01	0	1	2
Kalflex 14OA ®/Nexo(70:30)	4	5	5
Resiflex® K50	0	0.5	3
PLS Green® 9	4	4	5
DCS	0	1	3

0= good **5 = poor**

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
DINP		
 09077A/A4 DINP (palatinol N) - RE 1004 Sans rémelange - 0' remélange	 09077A/A4 DINP (Palatinol N) - RE 1004 1' remélange	 09077A/A4 DINP - (Palatinol N) - RE 1004 5' remélange
DEHP		
 09077A/A3 DEHP - RE 898 Sans rémelange - 0' remélange	 09077A/A3 DEHP - RE 898 1' remélange	 09077A/A3 DEHP - RE 898 5' 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
DIDP	10007A/1 DIDP - RE 812 Sans remélange	10007A/1 DIDP - RE 812 1' de remélange	10007A/1 DIDP - RE 812 5' de remélange
Polysorb® ID 37	10007A/5 Polysorb ID 37 - 2009-11-17/03 Sans remélange	10007A/5 Polysorb ID 37 - 2009-11-17/03 1'00" de remélange	10007A/5 Polysorb ID 37 - 2009-11-17/03 5'00" de remélange

Bio-based Plasticisers for PVC



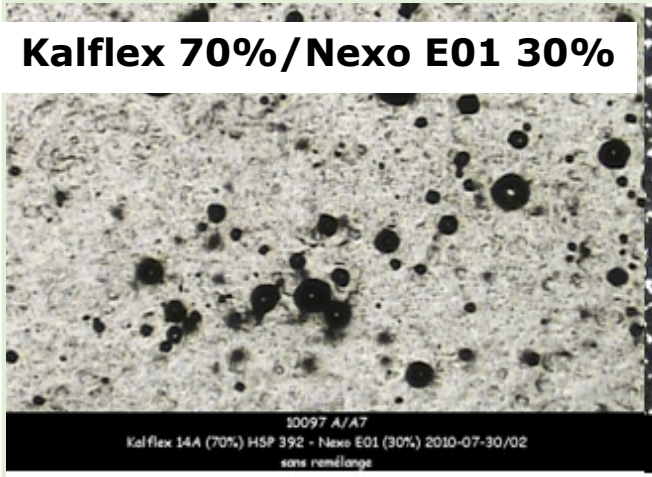
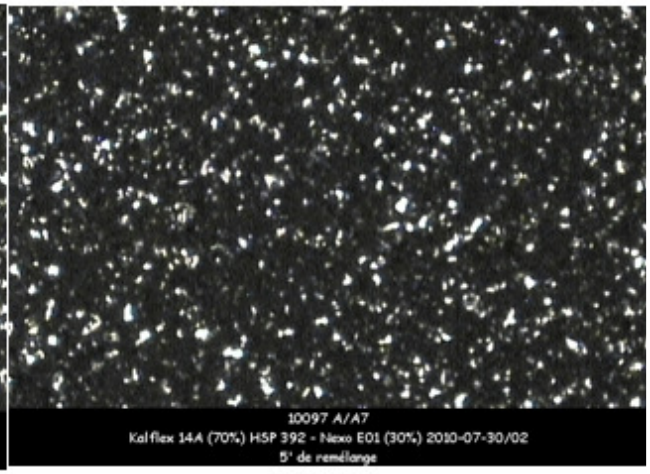
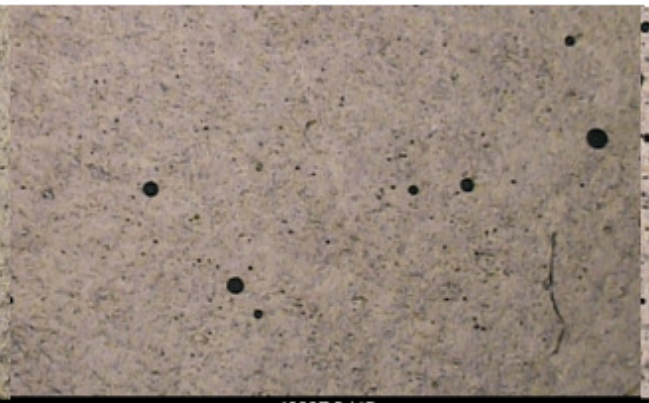
Transparent Paste PVC: Air Release & Air Entrapment

	after air removal	after 1 min of re-stirring	after 5 min of re-stirring
Soft-N-Safe	10007A/4 Soft_safe - 2009-10-12/01 Sans remélange	10007A/4 Soft_Safe - 2009-10-12/01 1' de remélange	10007A/4 Soft_Safe - 2009-10-12/01 5' de remélange
Nexo E01	10007A/6 NEXO E01 - 2010-01-27/20 Sans remélange	10007A/6 NEXO E01 - 2010-01-27/20 1'00" de remélange	10007A/6 NEXO E01 - 2010-01-27/20 5'00" de remélange

Bio-based Plasticisers for PVC



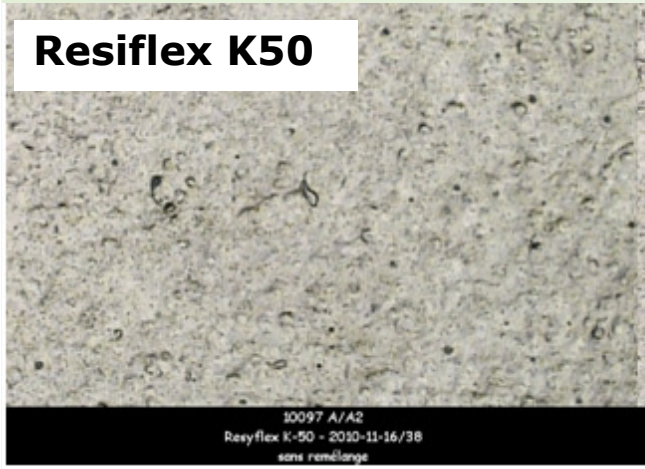
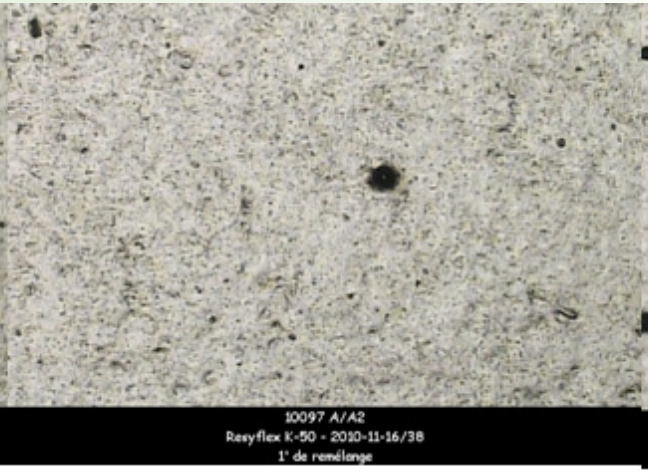
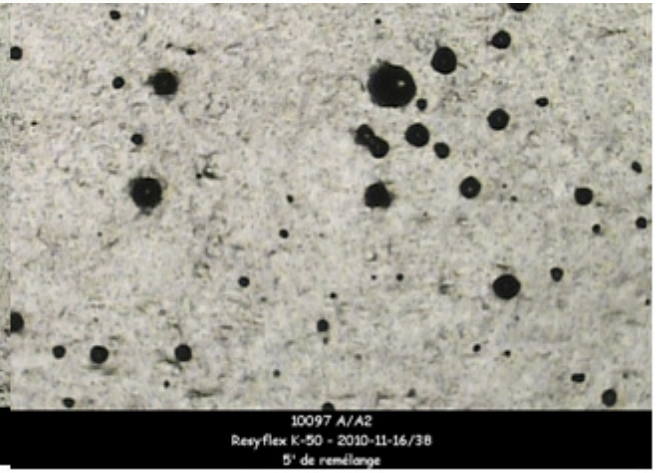
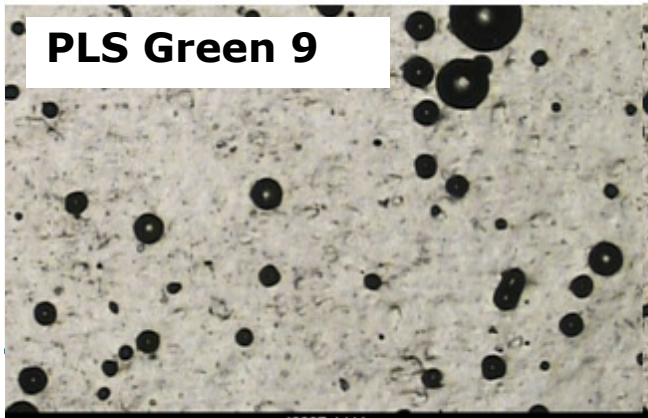
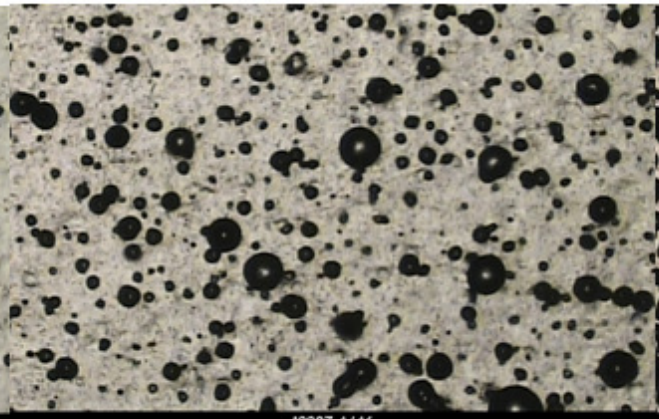
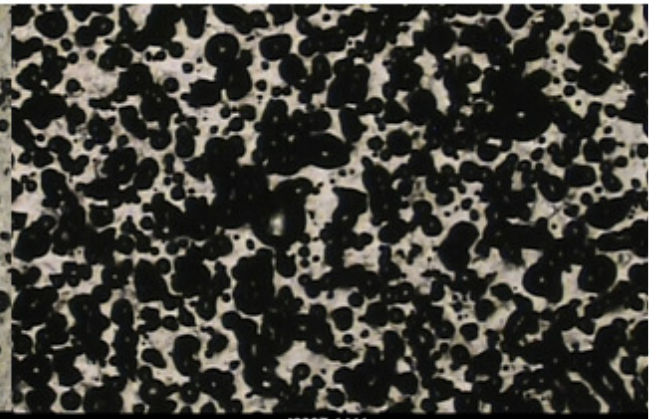
Transparent Paste PVC: Air Release & Air Entrapment

	after air removal	after 1 min of re-stirring	after 5 min of re-stirring
Kalflex 70%/Nexo E01 30%	 10097 A/A7 Kalflex 14A (70%) HSP 392 - Nexo E01 (30%) 2010-07-30/02 sans remélange	 10097 A/A7 Kalflex 14A (70%) HSP 392 - Nexo E01 (30%) 2010-07-30/02 1' de remélange	 10097 A/A7 Kalflex 14A (70%) HSP 392 - Nexo E01 (30%) 2010-07-30/02 5' de remélange
DCS	 10007 B/A5 Dicapryl sebacate (DCS) - Sans débullage 2010-03-30/09	 10007 B/A5 Dicapryl Sebacate (DCS) - 1' débullage 2010-03-30/09	 10007 B/A5 Dicapryl Sebacate (DCS) - 5' débullage 2010-03-30/09

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
Resiflex K50		
		
10097 A/A2 Resyflex K-50 - 2010-11-16/38 sans remélange	10097 A/A2 Resyflex K-50 - 2010-11-16/38 1' de remélange	10097 A/A2 Resyflex K-50 - 2010-11-16/38 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



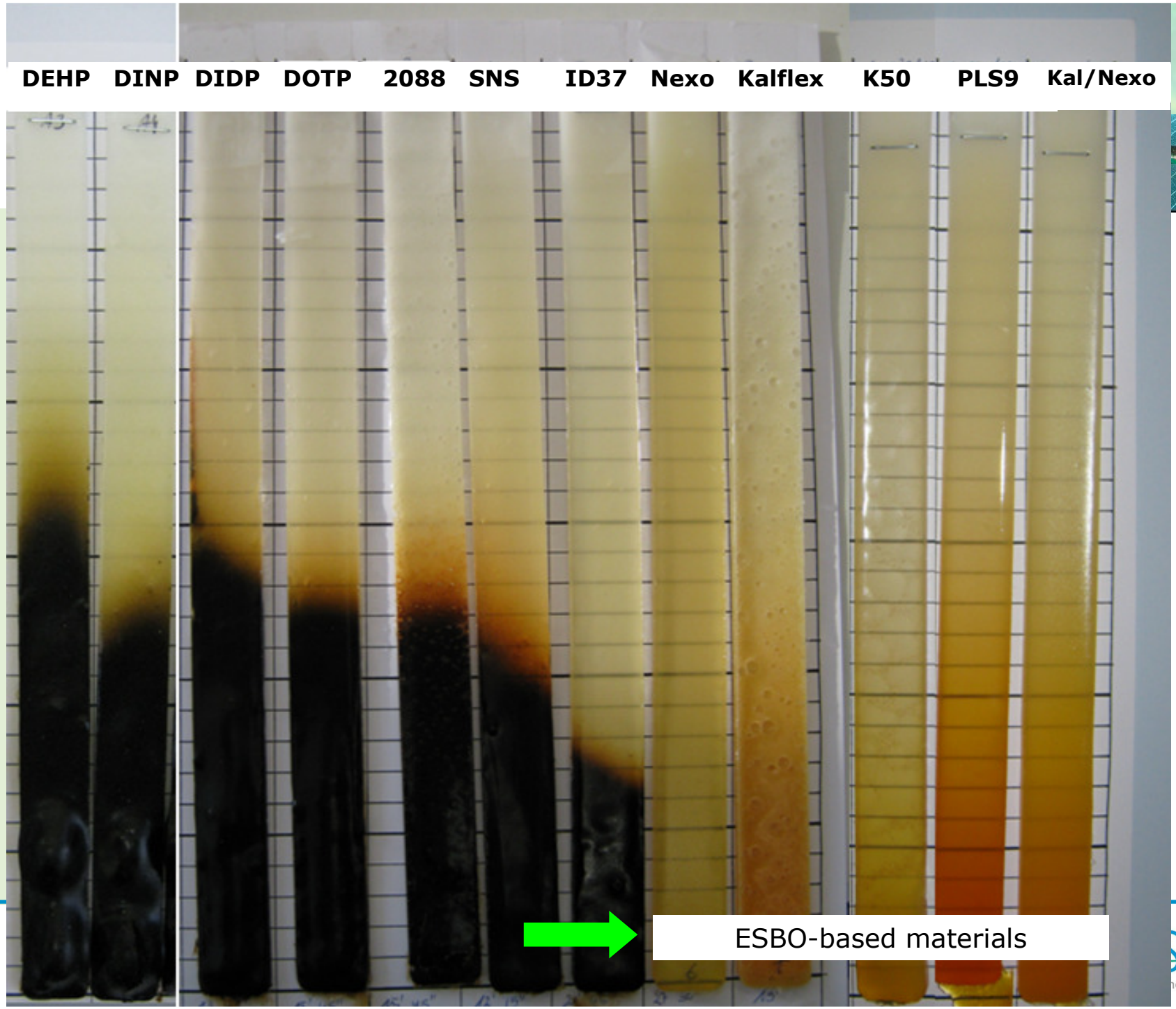
Transparent Paste PVC: Thermal Stability

- 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
Soft-N-Safe®	36	12
Polisorb® ID 37	38	21
Nexo E01	152	27
Kalflex ®/Nexo(70:30)	184	NM[2]
Resiflex® K50	NM[3]	NM[2]
PLS Green® 9	142	NM[2]
DCS	37	11

- ESBO-based materials (Nexo® E01, Kalflex® 14A, Resiflex® K50 and PLS Green® 9) 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
Nexo
Kalflex
K50
PLS9
Kal/Nexo
ESBO-based materials

Bio-based Plasticisers for PVC



Transparent Paste PVC: Colour, Gloss & Transparency of Films

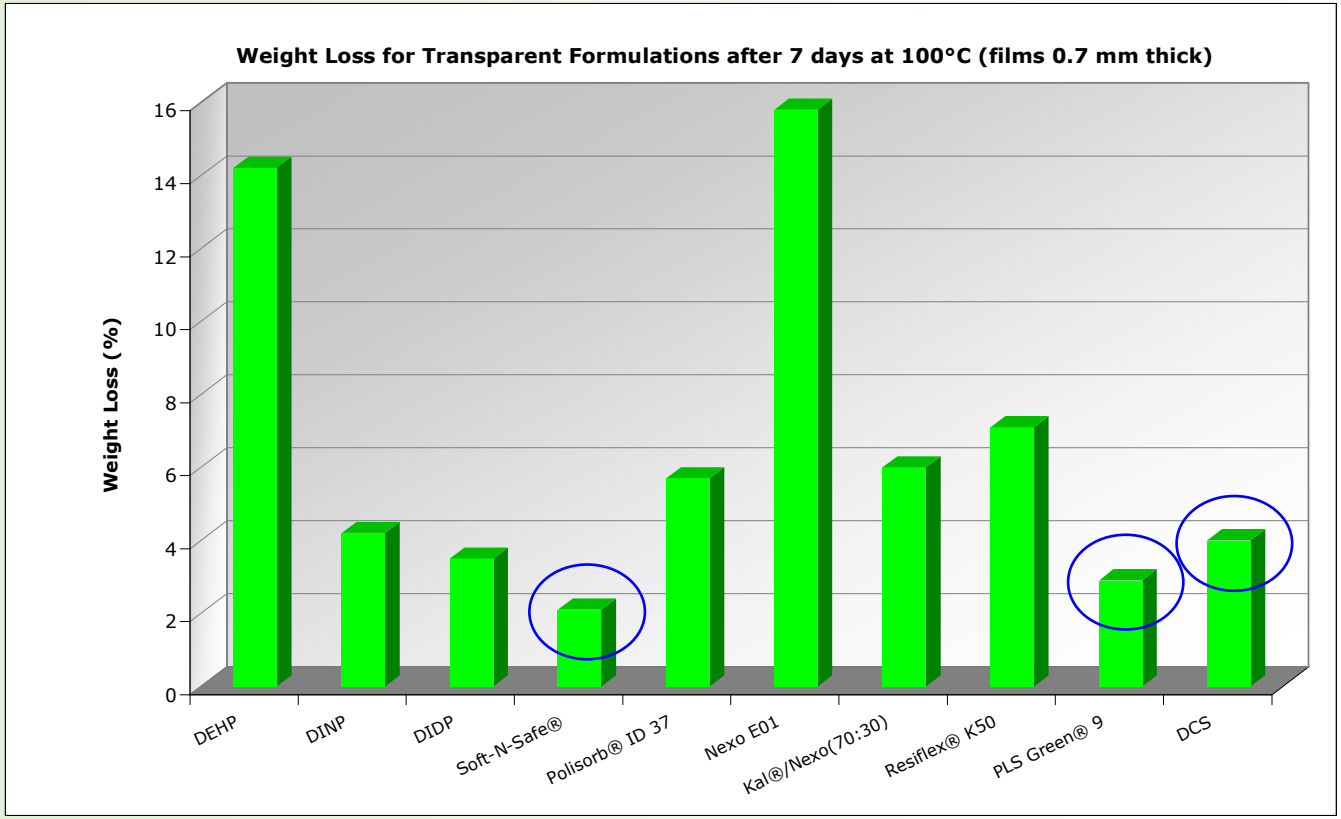
Plasticiser	Yellow Index	Gloss	Transparency
DEHP	8,1	25,6	78,9
DINP	7,4	27,7	86,1
DIDP	8,5	22,4	80,4
Soft-N-Safe®	8,4	21,9	73,1
Polysorb® ID 37	8,78	24,5	80,2
Nexo E01	17,8	22,6	74,1
Kalflex®/Nexo(70:30)	12,5	22,5	64,4
Resiflex® K50	12,82	25,1	77,8
PLS Green® 9	11,9	32,8	69
DCS	13,42	35	64,9

- ESBO-based materials (and DCS) are more yellowish than GP plasticisers;
- Soft-N-Safe and Polysorb ID 37 exhibit good colour;
- Kalflex®, PLS Green® 9 and DCS are less transparent than GP plasticisers

Bio-based Plasticisers for PVC



Transparent Paste PVC: Weight Loss of Films

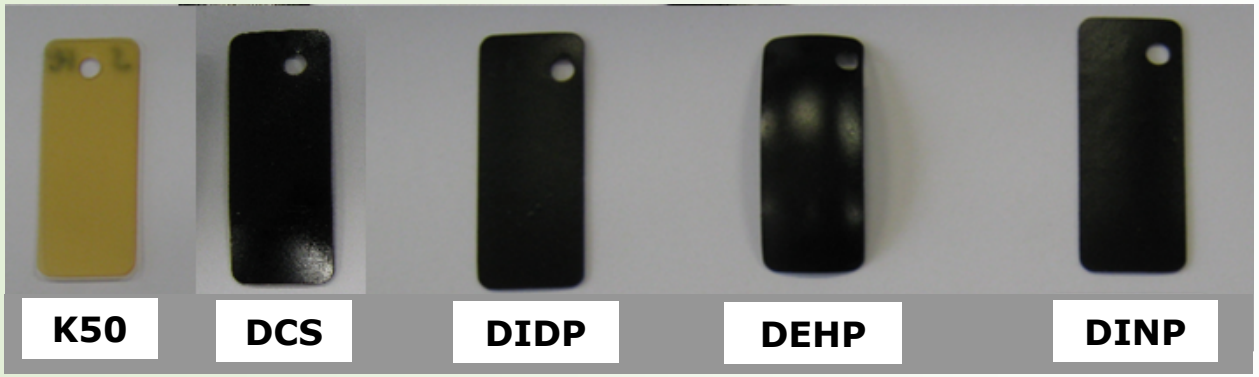


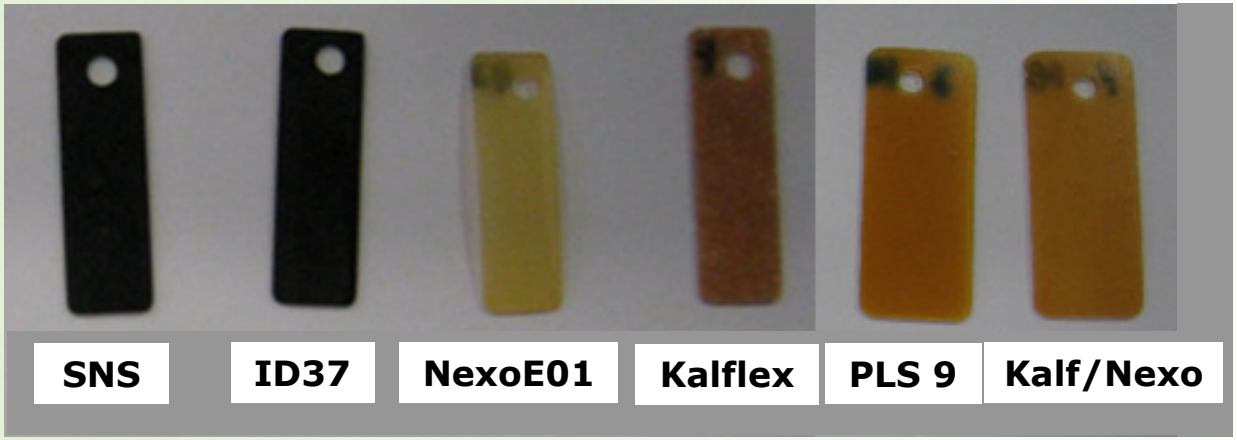
- Best results were obtained for Soft-N-Safe®, PLS Green® 9 and DCS. Kalflex alone is very good (~SNS). DCS exhibited strong exudation (greasy surface).

Bio-based Plasticisers for PVC



Transparent Paste PVC: Weight Loss of Films





100°C – 7 days
Films 0.7 mm thick

- All ESBO-based plasticisers presented good colour retention after 7 days: other materials were carbonised.

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	Air Release	T. Stability	Colour	Transp	Gloss	W. Loss	Score
DEHP	0/-	0/+	0	0	0	0/-	0	--	-2.5
DINP	0	0	0	0	0	0	0	0	0
DIDP	0/-	+	0/+	0	0	0/-	0/-	0/+	0.5
Soft-N-Safe®	--	0/-	0	0/+	0	0/-	0/-	+	-2
Polysorb® ID 37	0	++	+	+	0	0/-	0	-	2.5
Nexo E01	+	++	++	++	--	0/-	0/-	--	2
Kalflex®/Nexo(70:30)	-	+	-	++	-	-	0/-	-	-2.5
Resiflex® K50	+	++	++	+++	-	0/-	0	-	5.5
PLS Green® 9	+	++	-	++	-	-	+	+	4
DCS	--	+	++	0/+	-	-	+	0	0.5

- **Resiflex® K50**, **PLS Green® 9**, **Polysorb® ID 37** and **Nexo® E01** obtained the highest scores and can be considered (from the technical point-of-view) promising alternatives to GP plasticisers in simple transparent formulations;



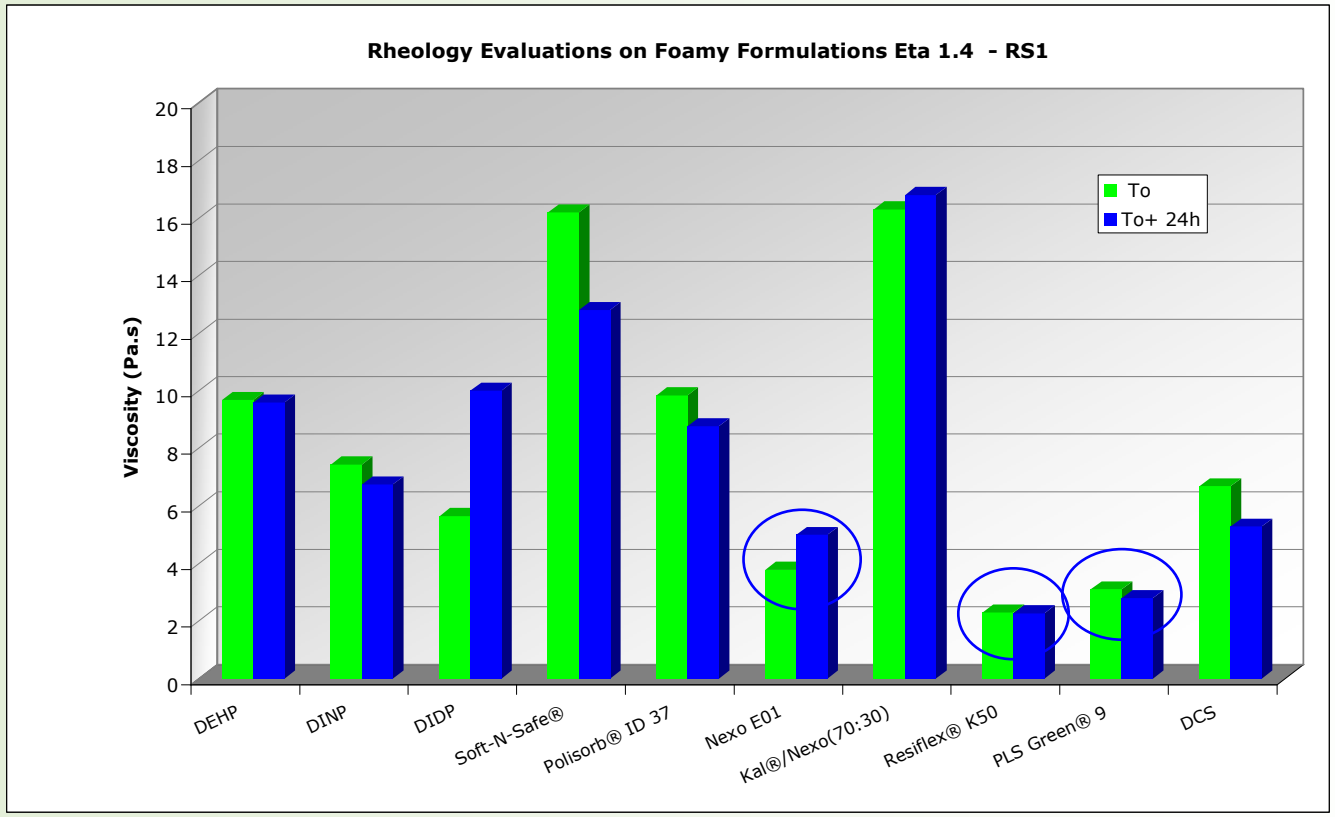
Experimental - Part 2

Foamy Layers Evaluations

Bio-based Plasticisers for PVC



Foamy Paste PVC: Viscosity & Paste Ageing

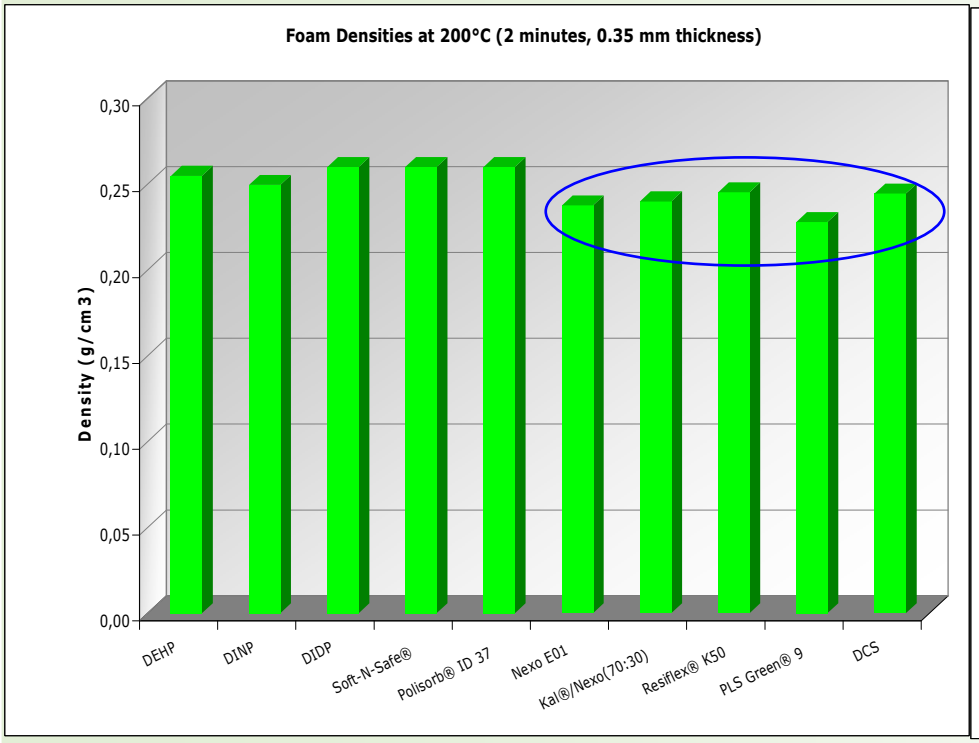


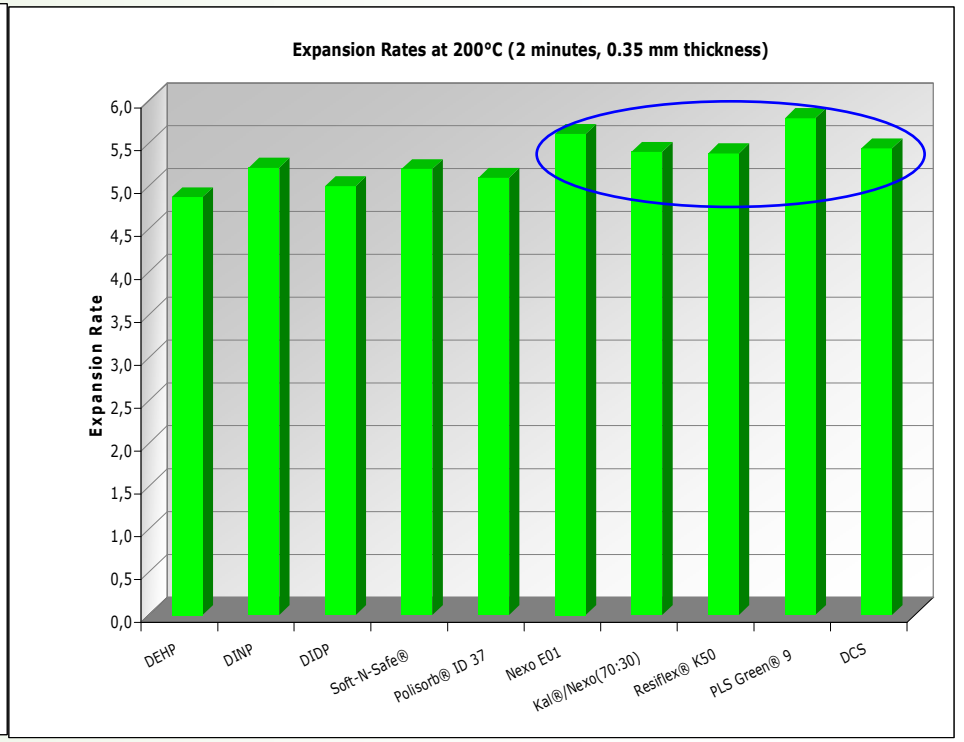
- Lowest viscosities were obtained for ESBO-based plasticisers K(50, PLS9 and Nexo E01. DCS had similar performance with regards to DINP, but with improved ageing

Bio-based Plasticisers for PVC



Foamy Paste PVC: Density & Expansion Ratio





- Generally speaking, bio-based plasticisers (Nexo® E01, Resiflex® K50, Kalflex® 14A, PLS Green® 9 and DCS) expand faster than GP plasticisers and therefore present slightly lower densities

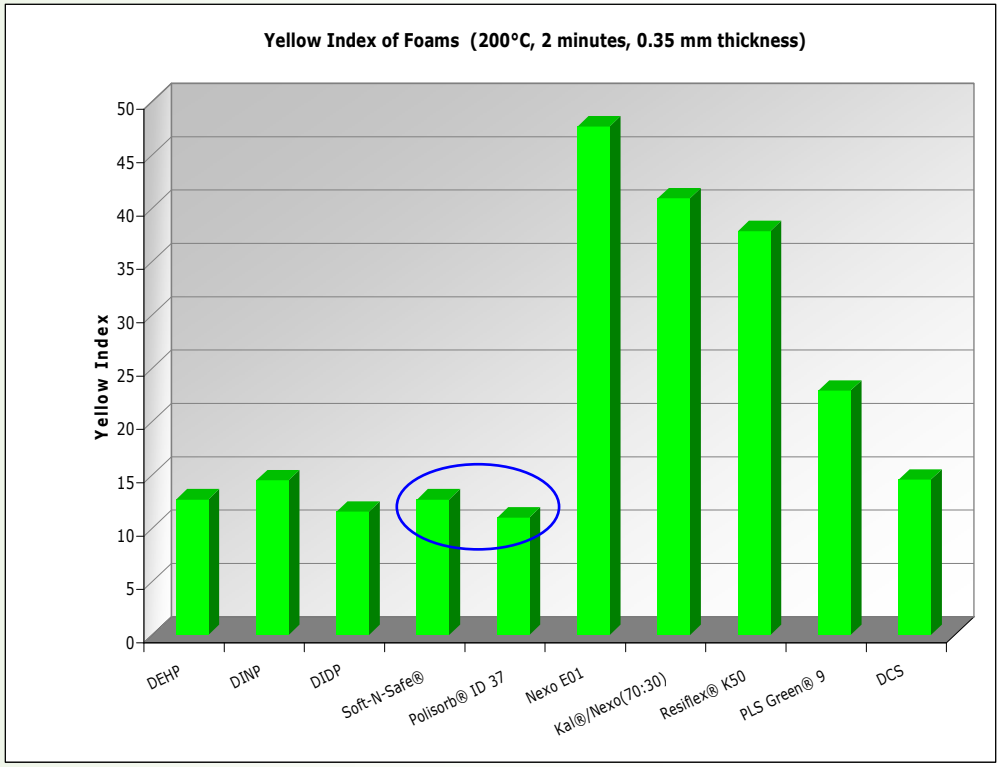
Bio-based Plasticisers for PVC



Foamy Paste PVC: Foam Quality & Colour

Plasticiser	Cell Quality (visual)
DEHP	very good
DINP	very good
DIDP	very good
Soft-N-Safe®	very good
Polisorb® ID 37	good
Nexo E01	medium
Kalflex®/Nexo(70:30)	good
Resiflex® K50	very good
PLS Green® 9	medium
DCS	good

- Cell qualities of Soft-N-Safe® and Resiflex® K50 are comparable to those of GP plasticisers



- Soft-N-Safe® and Polysorb® ID 37 exhibited good colour in comparison with GP phthalates. All the other 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
Soft-N-Safe®	-	0	0/+	0/-	0	0	-1
Polisorb® ID 37	0/-	0	0/+	0/-	0	0/-	-1
Nexo E01	+	0/-	--	0/+	++	-	0
Kalflex®/Nexo(70:30)	-	0	--	0/+	+	0/-	-2
Resiflex® K50	+	0	--	0	+	0	0
PLS Green® 9	+	0	-	+	++	-	2
DCS	0	0	0	0/+	+	0/-	1

- **PLS Green® 9**, **DCS, Resiflex® K50** and **Nexo® E01** are promising alternatives to GP plasticisers in foamy formulations. **Polysorb® ID 37** and **Soft-N-Safe®** are also good candidates, especially where there is a need for good colour and higher permanence.

Bio-based Plasticisers for PVC



Paste PVC Formulations: Overall Performance

Plasticiser	Score Transparent Layers	Score Foamy Layers	Total Score
DEHP	-2.5	-1	-3.5
DINP	0	0	0
DIDP	0.5	-1	-0.5
Soft-N-Safe®	-2	-1	-3
Polisorb® ID 37	2.5	-1	1.5
Nexo E01	2	0	2
Kalflex®/Nexo(70:30)	-2.5	-2	-4.5
Resiflex® K50	5.5	0	5.5
PLS Green® 9	4	2	6
DCS	0.5	1	1.5

- **Resiflex® K50, PLS Green® 9**, **Polysorb® ID 37, Nexo® E01** and **DCS** are promising alternatives to GP plasticisers in paste PVC formulations

Bio-based Plasticisers for PVC



Conclusions

- In the overall balance, **Resiflex® K50, PLS Green® 9** and **Polysorb® ID 37** are promising alternatives to GP plasticisers;
- **DCS** is an interesting candidate, but migration issues have to be taken into consideration;
- **Nexo® E01** performed well in average, but colour is still an issue and weight loss is strong. Actually this plasticiser would be better classified as a **fast fusing**;
- Where there is a special need for good colour and higher permanence, **Soft-N-Safe®** is an excellent candidate;
- Where there is a special need for good thermal stability and higher permanence, **Kalflex® 14OA** is an excellent candidate. Viscosity, nevertheless, has to be lowered;

Bio-based Plasticisers for PVC



Conclusions

- Generally speaking, ESBO-based plasticisers are more yellowish than GP phthalates and also present outstanding thermal stability;
- Blends with these different plasticisers searching for possible synergies were not taken into consideration in this work but can offer promising results. It's the case of Kalflex and Nexo E01 blended with DINP, for example;
- On the other hand, additional evaluations in production lines and in more complex formulations are necessary for further performance validation;
- Also, this assessment took into consideration mostly the **technical** point of view and **not** the **toxicological** and **commercia**l ones (prices and availability), aspects that play a major role on the choice of a given plasticiser;
- And most important: SolVin resins work pretty well with all these bio-based plasticisers!

Thanks for your attention!

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