Oxoviflex® – results of application tests in PVC formulations

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Plasticisers

Applications:

- *Esters of aliphatic dicarboxylic acids*: in mixtures with phthalates, to improve impact strength of soft PVC products at reduced temperatures.
- *Phosphates*: obtaining technical articles with reduced flammability.
- *Phenolic esters of alkyl sulphonic acids:* minimum volatility, good resistance to ageing in atmospheric conditions despite slight yellowing.
- *Citrates*: special softeners for certain products complying with the requirements of regulations regarding direct contact with food.
- *Trimellitates:* intended for products exposed to prolonged influence of elevated temperatures.

- *Epoxy products: (PVC-P)* co-plasticising effect; if used in larger amounts with no other substance added, exudation may occur.
- *Polyester, oligomeric and polymeric softeners:* apart from their reduced volatility, they are characterised by good resistance to extraction by fats, oils and fuels.

Restrictions

Restrictions on using PVC additives

Plasticisers
Directive 2005/84/EC
DEHP, DBP, BBP

➢relating to the classification, packaging and labelling of dangerous substances identified as reprotoxic substances and have therefore been classified as reprotoxic, category 2.

DINP, DIDP, DNOP

➢scientific information is either lacking or conflictual, but it cannot be excluded that they pose a potential risk if used in toys and childcare articles, which are by definition produced for children.

Stabilisers

Directive 67/548/EEC

Pb, Cd

➢ relating to the classification, packaging and labelling of dangerous materials

- most Pb compounds have been categorised as causing adverse reproductive effects, as being harmful to health, dangerous for the environment and as involving the risk of cumulative effects Pb and Cd resistant to biodegradation

- Cd compounds have been categorised as being harmful to health and dangerous for the environment, others as toxic or very toxic (carcinogenic, category 2)

(Cd: directive 91/338/EEC)

Restrictions

"**DEHP, DBP, BBP** – shall not be used as substances or as constituents of preparations, at concentrations of greater than 0.1% by mass of the plasticised material, in toys and childcare articles. Such toys and childcare articles containing these phthalates in a concentration greater than the limit mentioned above shall not be placed on the market."

"**DINP, DIDP, DNOP** – shall not be used as substances or as constituents of preparations, at concentrations of greater than 0.1% by mass of the plasticised material, in toys and childcare articles which can be placed in the mouth by children. Such toys and childcare articles containing these phthalates in a concentration greater than the limit mentioned above shall not be placed on the market."

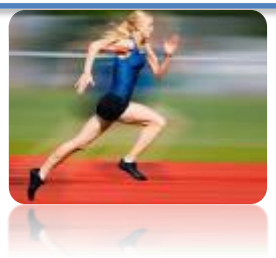
Type of PVC	Type of additive	Specific migration limit (mg/kg)
PVC-U	Organotin stabiliser (monooctyl compounds)	1.2
PVC-U	Organotin stabiliser (dioctyl compounds)	0.04
PVC-P	DEHA plasticiser – monomeric – polymeric	18 30

Maximum levels of specific migration of certain additives used in PVC articles (directive 2002/72/EC).

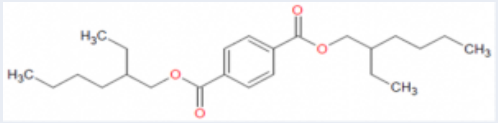
New trends in PVC plasticising

Solution ➡ phthalate-free plasticisers

Company	Plasticiser
Grupa Azoty ZAK S.A.	**Oxoviflex™ – DEHT – bis(2-ethylhexyl) ester of benzene-1,4-dicarboxylate acid→ alternative for phthalates, used in the production of sheet flooring, vinyl wallpapers, flexible (sanitary) pipes, electrical conduits, cable coatings, artificial leather, films and packaging, PVC coatings, products for children, etc.**
BASF	**Hexamoll DINCH** – toxicologically neutral, used in products for children (listed in 2002/72/EC, a slight correction in terms of formulation chemistry)
Eastman	**Eastman 168 (DEHT)** – used, among others, in the production of toys, childcare articles, medical equipment and many more **Benzoflex** – a benzoic acid derivative (production of adhesives, sealants and sheet flooring)
Lanxsess	**Mesamoll TP** – used in the production of sheet flooring, panelling → alternative for DBP and BBP
Perstrop	**Pevalen** – a polyester plasticiser, developed for sensitive applications, suitable for products coming into direct contact with skin (sheet flooring, coated fabrics and toys)



DEHT – the fastest-growing plasticiser in Europe

General characteristics		
Substance	bis(2-ethylhexyl) ester of benzene-1,4-dicarboxylate acid	
Production	2-ethylhexyl alcohol + PTA	DEHT
REACH	Registered	No application restrictions

The aim of the study was to assess new non-phthalate **PVC** plasticisers such as ***OXOVIFLEX (OXO) and bis(2-ethylhexyl) biosuccinate (BDO)*** compared with **DEHP and DINP** bis(2-ethylhexyl) biosuccinate plasticisers and to develop framework formulations containing the listed plasticizers

❖ Comparative studies of the properties of the tested plasticisers compared to conventional plasticisers have been carried out;

❖ Mixtures of suspension PVC and varying content of the tested plasticisers have been prepared, and moulded pieces made of them were then tested in terms of their physical and mechanical properties;

❖ Pastes of emulsion PVC and varying content of the tested plasticisers have been prepared, and coatings made of them were then tested in terms of their physical and mechanical properties.

Testing new plasticisers

Plasticisers:

- determination of volatile matter;
- thermogravimetric analysis in a full temperature range;
- absorption of plasticisers at room temperature.

Mixtures:

PVC mixtures prepared in a hot and cold high-shear mixer; number of stirrer rotations in a hot mixer – 1,500 r.p.m., and in a cold mixer – approximately 450 r.p.m.

- Shore hardness: A;
- water absorption after 1 and 7 days (PN-EN ISO 62:2000);
- loss of weight (150, 160, 170, 180°C);
- migration of plasticiser after 1, 3 and 7 days (PN-EN ISO 177:2003);
- tensile strength and relative elongation at break (PN-EN ISO 527-2:1998);
- tear resistance (PN-EN ISO 6383-1:2005).

Pastes:

➢ determination of viscosity of pastes using the *Brookfield* method after 1, 3 and 168 h;

Pastes have been gelled at T = 150°C in t = 15 minutes

Types of plastisol tests

➢water absorption after 1 and 7 days;
➢loss of weight;
➢migration of plasticiser after 1, 3 and 7 days;
➢tensile strength and relative elongation at break;
➢tear resistance.

Volatility (130°C, 3 h)

Oxoviflex – 0.07%

BDO – 1.2%

Raw materials

Mixtures:

- ✓S-70 suspension polyvinyl chloride;
- ✓plasticisers; OXO, BDO, DINP and DEHP;
- ✓premium precipitated chalk;
- ✓Ca/Zn BP MC 8656 KA–ST “BEARLOCHER” stabiliser;
- ✓epoxy soybean oil – prod. Chemtura (Brenntag);
- ✓microwax;
- ✓antioxidant (phenolic derivative).

Raw materials

Pastes:

- ✓emulsion polyvinyl chloride – SABIC 703 (Brenntag);
- ✓ plasticisers; OXO, BDO, DINP and DEHP;
- ✓ epoxy soybean oil – prod. Chemtura (Brenntag);
- ✓ Lancromark LZC 393 stabiliser – prod. Akcros Chemicals;
- ✓ BYK 3160 de-areator;
- ✓VISCOBYK 5100 viscosity reducer.

Mixture formulations

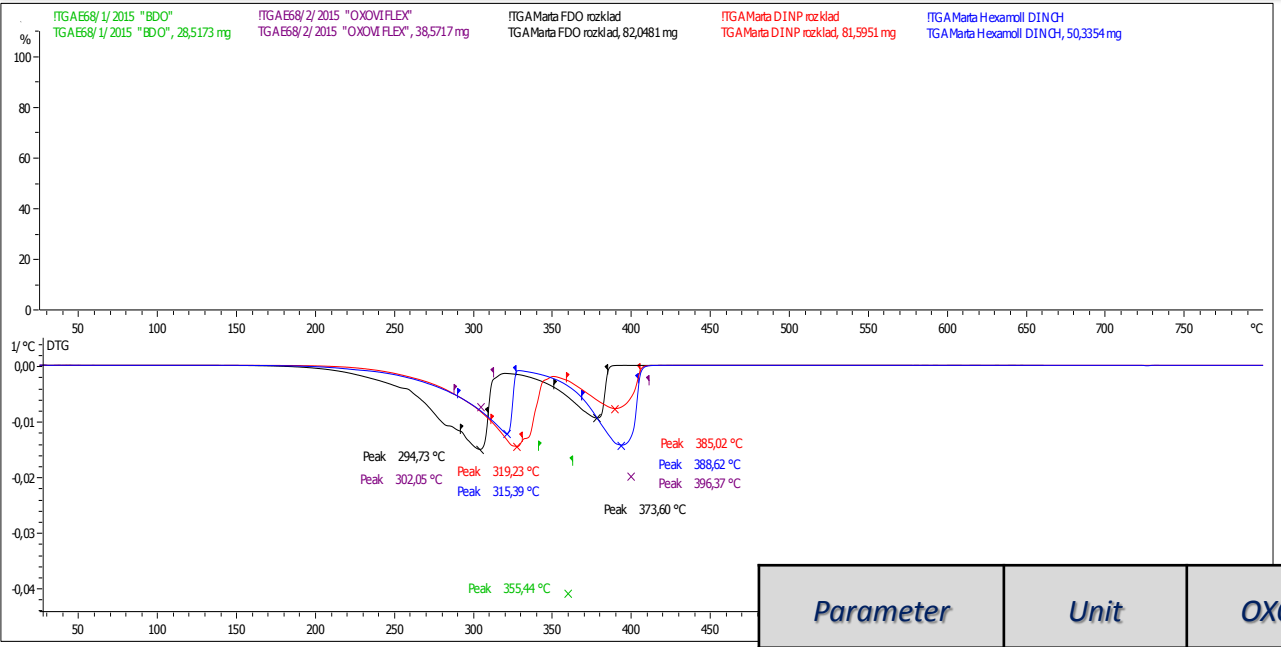
No.	Mixture Ingredients Part by mass	OXO EX/1		BDO EX/1		DEHP EX/1		DINP EX/1	
1.	PVC S70	100		100		100		100	
2.	Plasticiser	50	70	50	70	50	70	50	70
3.	Premium chalk 1	10		10		10		10	
4.	Ca/Zn stabiliser BPMC 8656 KA-ST	4.5		4.5		4.5		4.5	
5.	Antioxidant	0.3		0.3		0.3		0.3	
				.15		0.15		0.15	

No.	Mixture Ingredients Part by mass	OXO EX/2		BDO EX/2		DEHP EX/2		DINP EX/2	
1.	PVC S70	100		100		100		100	
2.	Plasticiser	50	70	50	70	50	70	50	70
3.	Premium chalk 1	10		10		10		10	
4.	Ca/Zn stabiliser BPMC 8656 KA-ST	4.5		4.5		4.5		4.5	
5.	ESBO soybean oil	2.5		2.5		2.5		2.5	
6.	Antioxidant	0.15		0.15		0.15		0.15	

Paste formulations

Sample No.	PVC-E	OXO	BDO	DINP	DEHP	Ca/Zn stab.	Epoxy soybean oil	De-areator	Viscosity reducer
1	100	50	-	-		3	3	1	0.7
2	100	-	50	-	-	3	3	1	0.7
3	100	-	-	50	-	3	3	1	0.7
4	100				50	3	3	1	0.7
5	100	70				3	3	1	0.7
6	100		70			3	3	1	0.7
7	100			70		3	3	1	0.7
8	100				70	3	3	1	0.7
9	100	90				3	3	1	0.7
10	100		90			3	3	1	0.7
11	100			90		3	3	1	0.7
12	100				90	3	3	1	0.7

Results of tests on plasticisers



Laboratorium Analizy Termicznej: METTLER

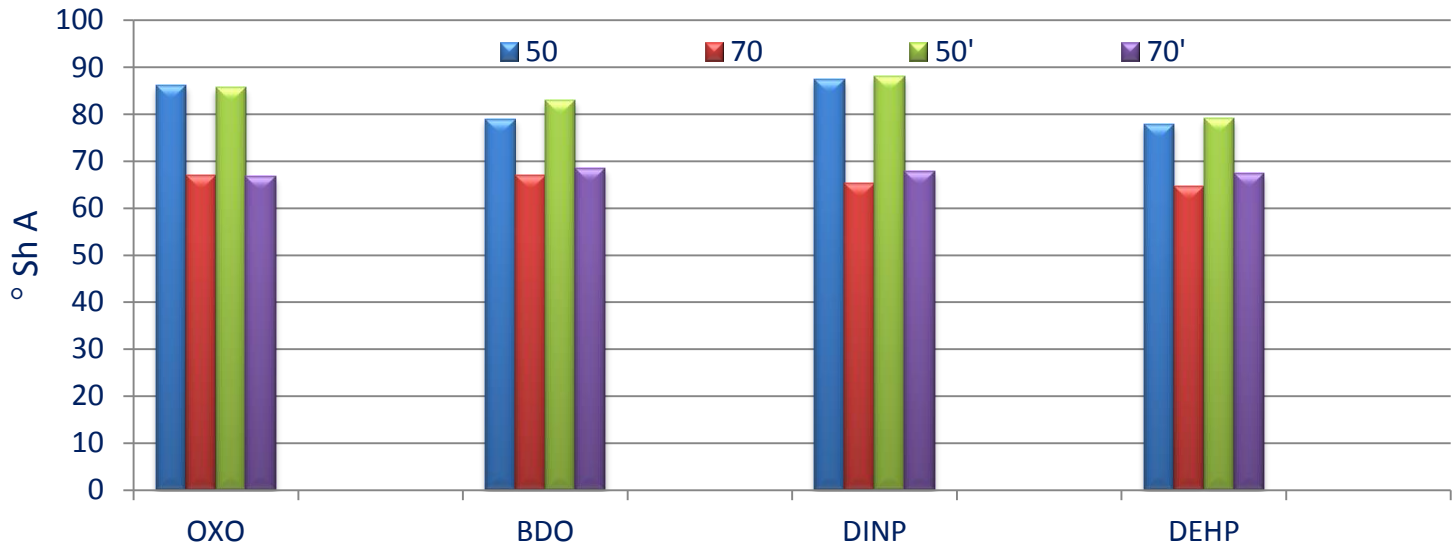
Presentation of TGA thermograms for the tested plasticisers

Thermogravimetric analysis

Parameter	*Unit*	*OXO*	*BDO*	*DINP*	*DEHP*
Decomposition temperature I	°C	302.05	355.44	319.23	294.73
Decomposition % I	%	29.19	99.84	71.37	68.43
Decomposition temperature II	°C	396.37	-	385.02	373.60
Decomposition % II	%	70.56	-	28.12	30.80
Decomposition product	%	0.13	0.03	0.25	0.77

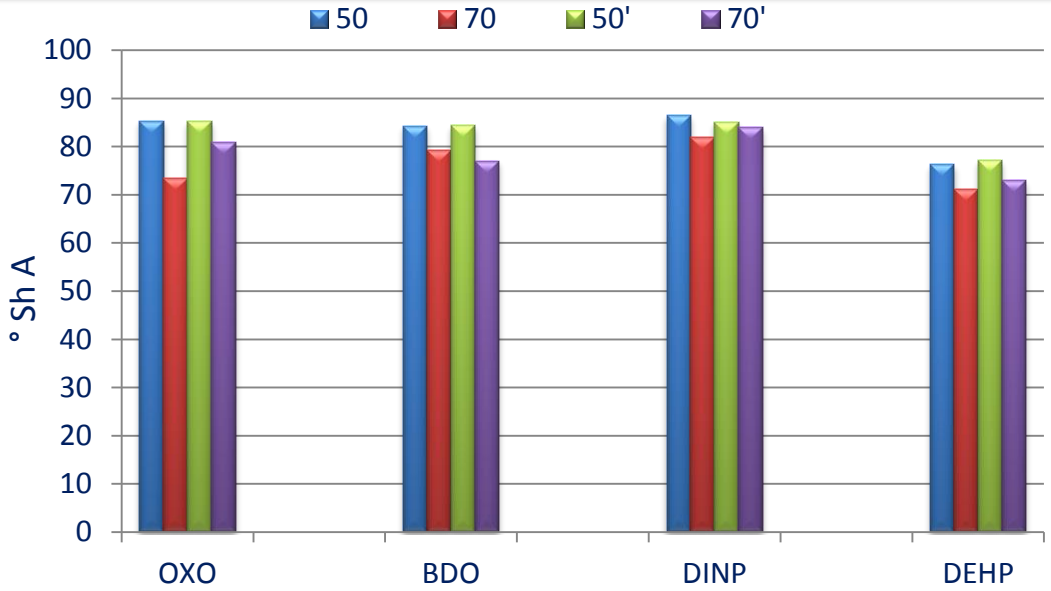
Results of physical and mechanical tests of moulded pieces made of the prepared mixtures

Results of tests on mixtures – hardness



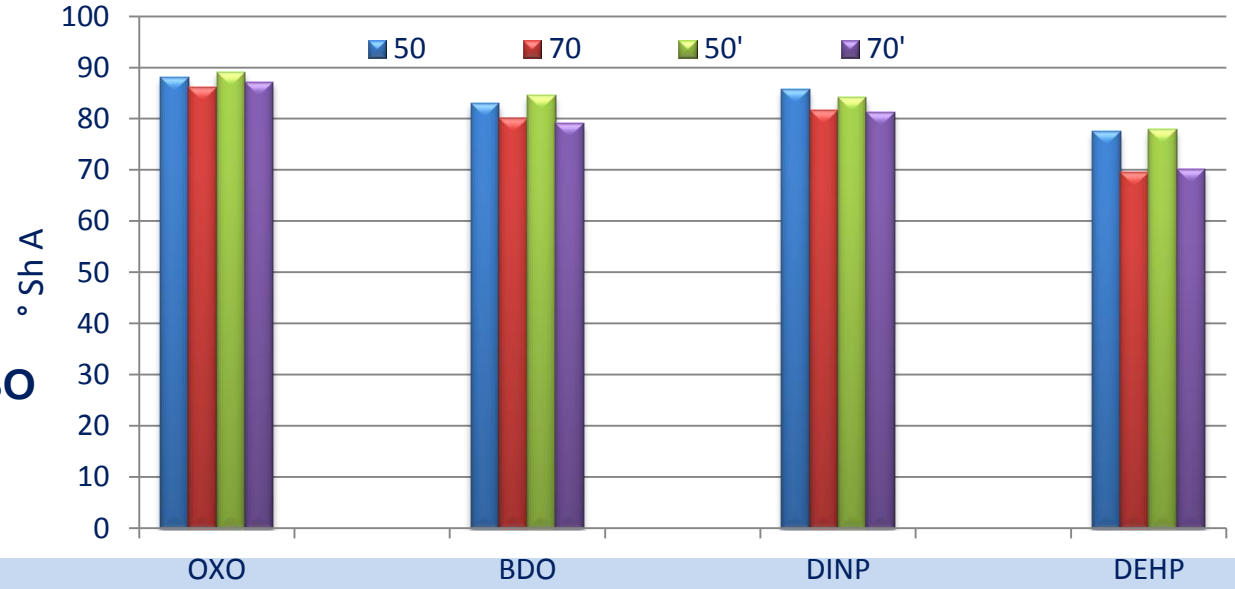
mixtures without additives

Results of tests on mixtures – hardness

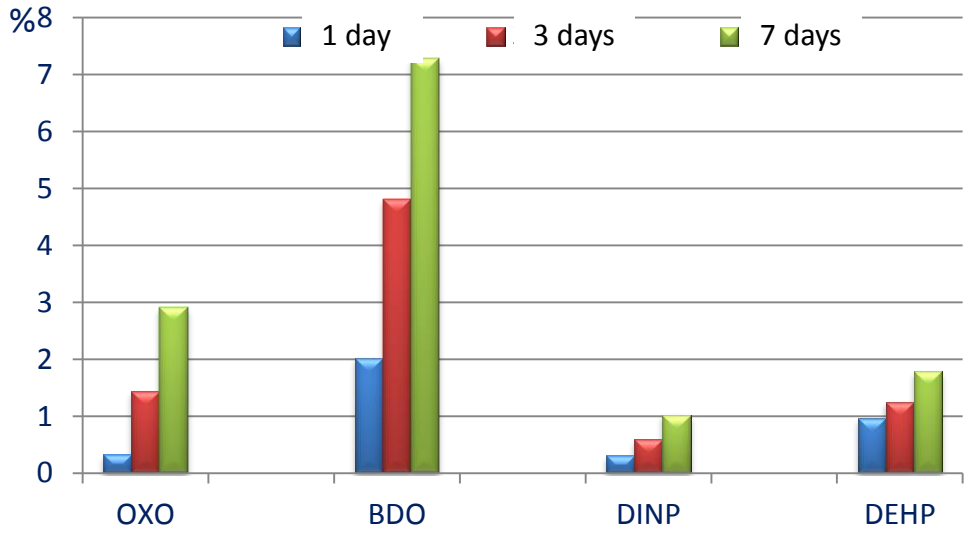


Mixtures with chalk and microwax

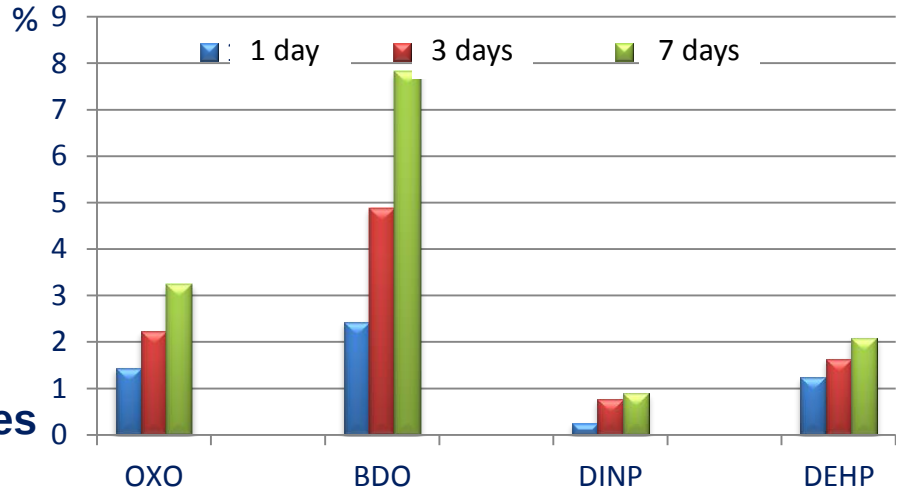
Mixtures with chalk and ESBO



Results of tests on mixtures – migration

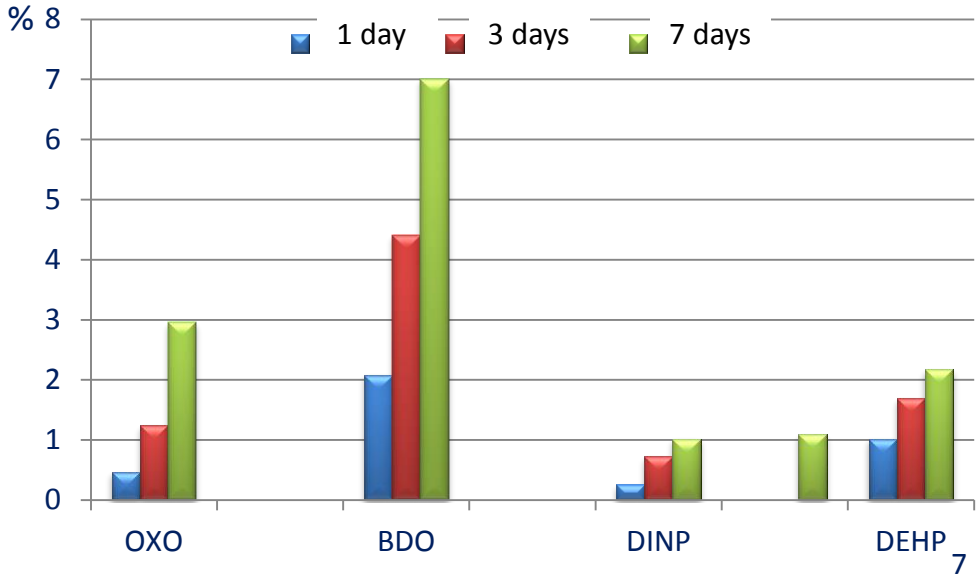


50 parts of plasticiser without additives

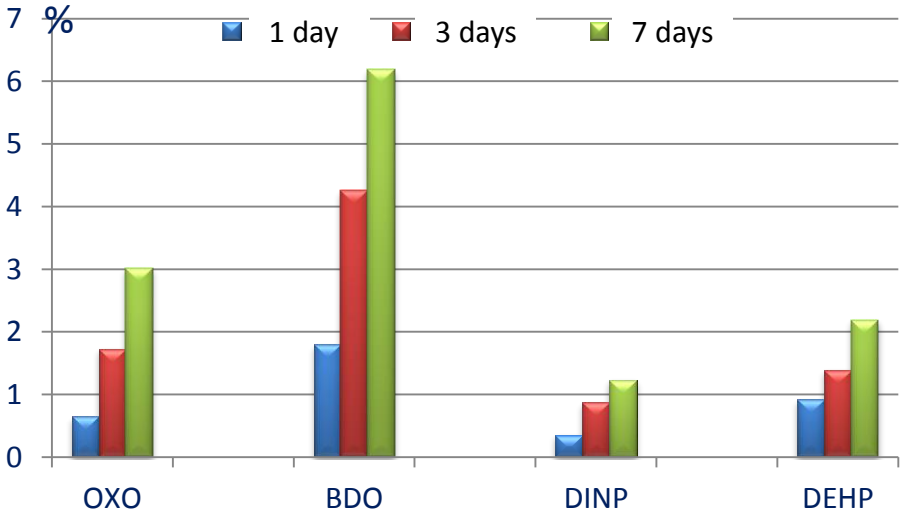


70 parts of plasticiser without additives

Results of tests on mixtures – migration

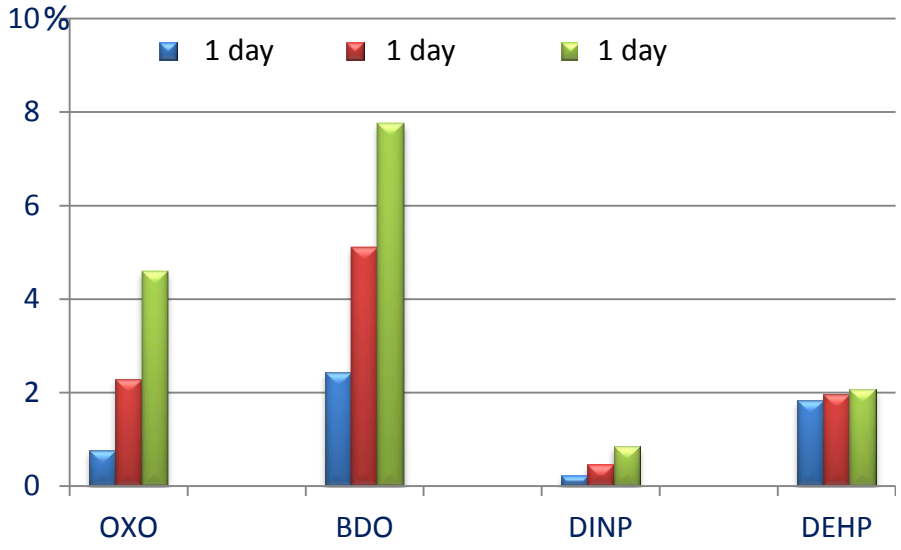


50 parts of plasticiser with chalk and microwax

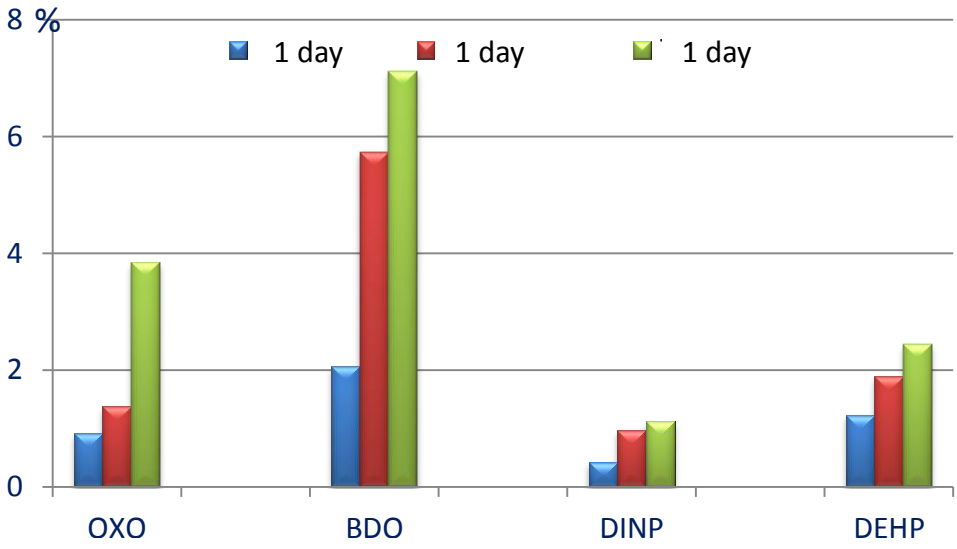


50 parts of plasticiser with chalk and ESBO

Results of tests on mixtures – migration

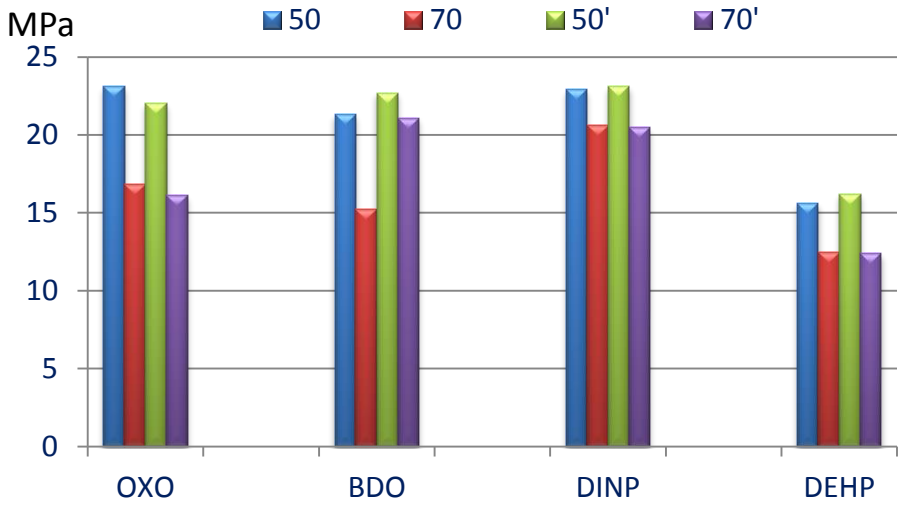


70 parts of plasticiser with chalk and microwax

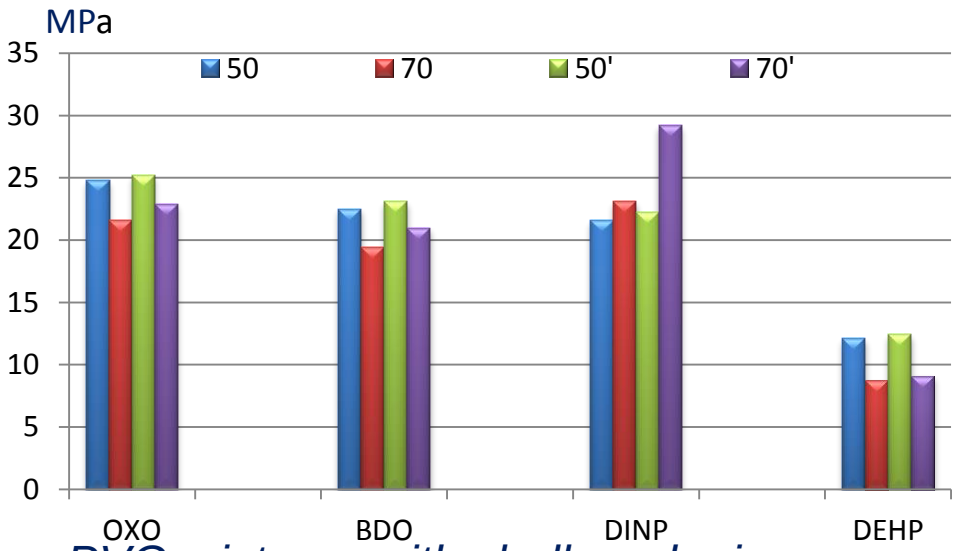


70 parts of plasticiser with chalk and ESBO

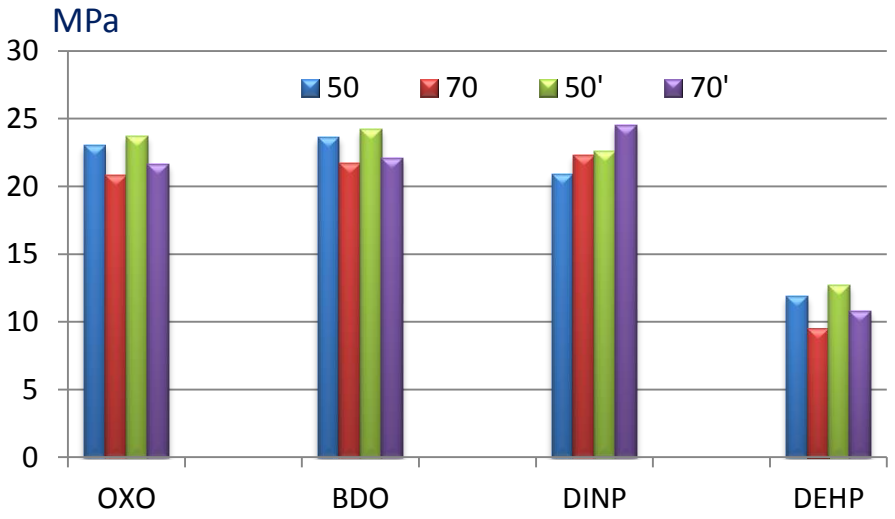
Results of tests on mixtures – tensile strength



PVC mixtures without additives

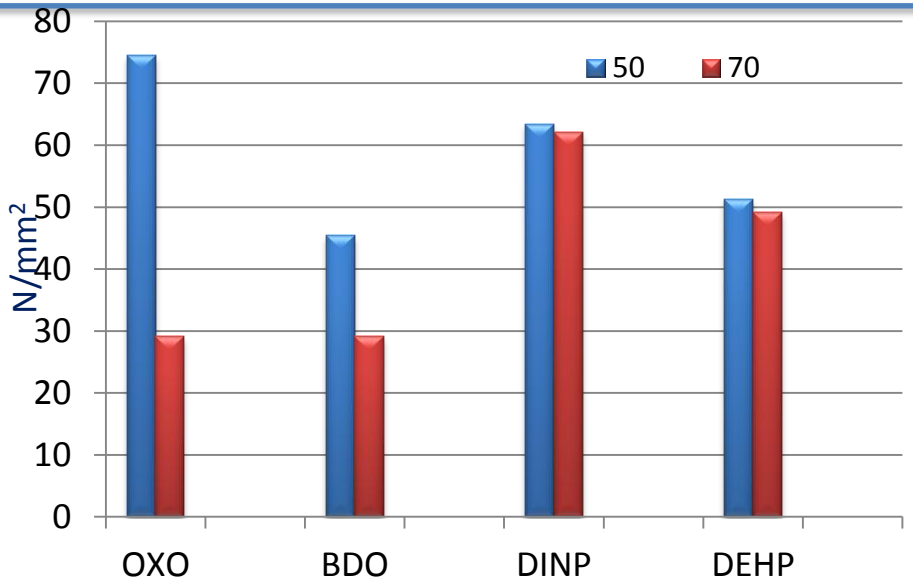


PVC mixtures with chalk and microwax

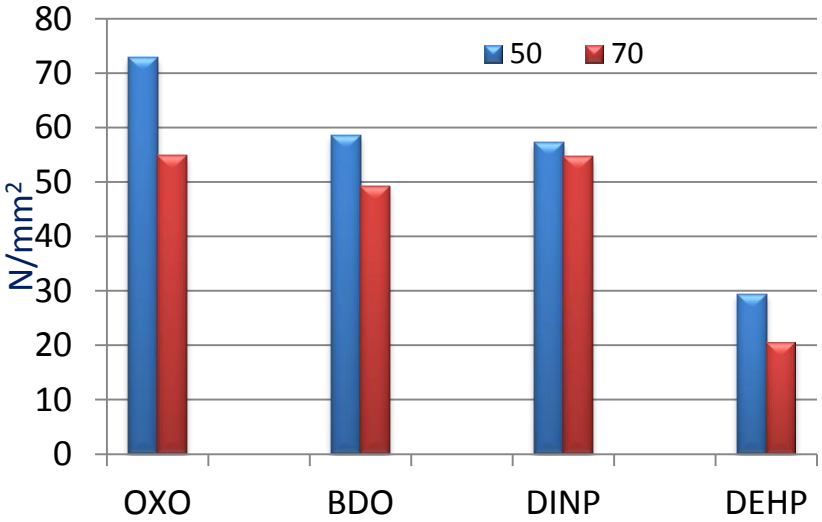


PVC mixtures with chalk and ESBO

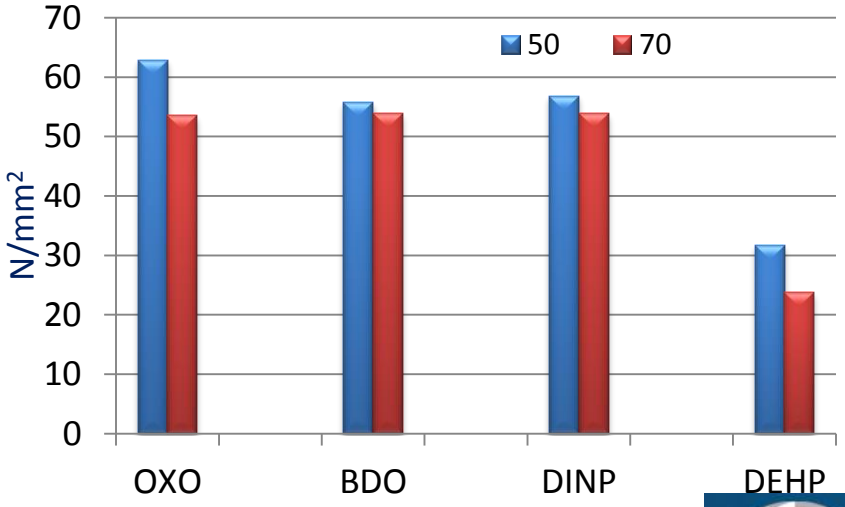
Results of tests on mixtures – tear resistance



PVC mixtures without additives



PVC mixtures with chalk and microwax

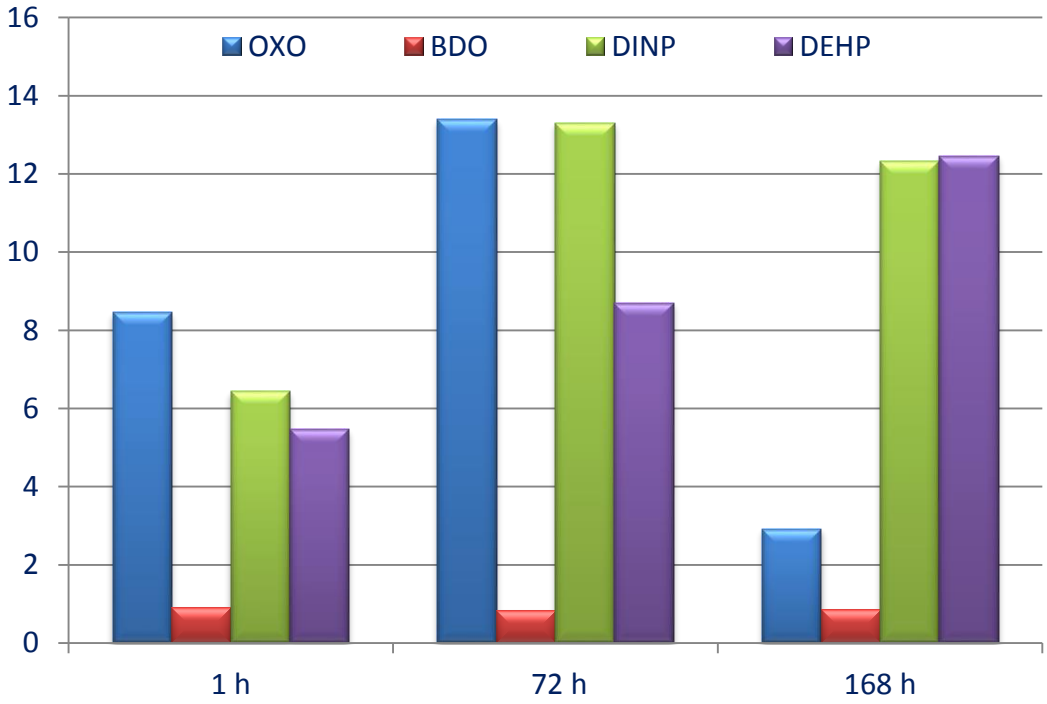


PVC mixtures with chalk and ESBO

Results of physical and mechanical tests of plastisol coatings

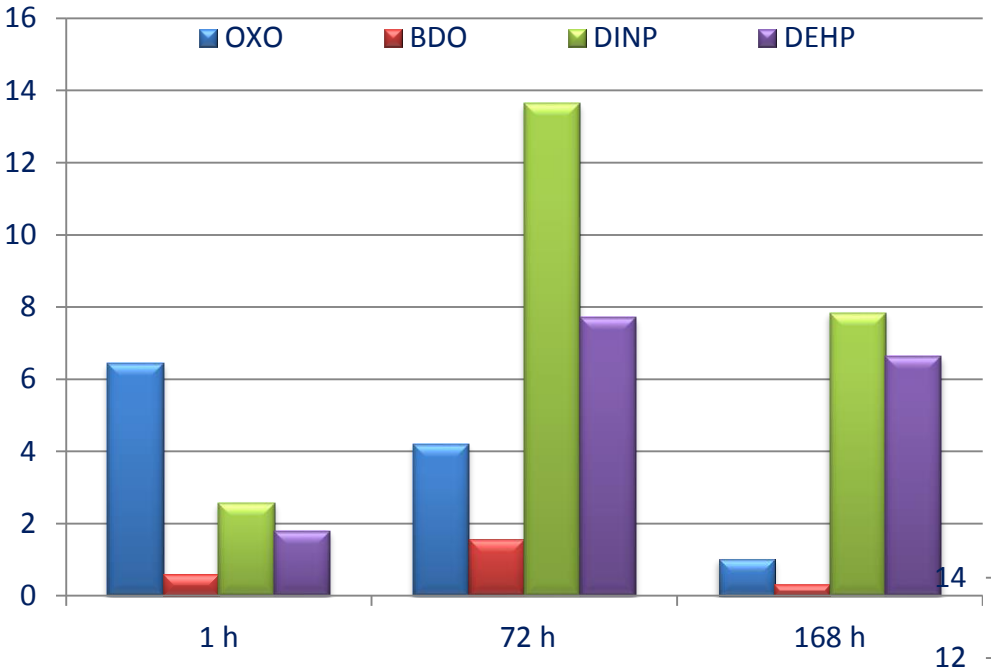
Results of tests on pastes

Determination of apparent viscosity using the Brookfield method (PN-ISO 2555:1999)



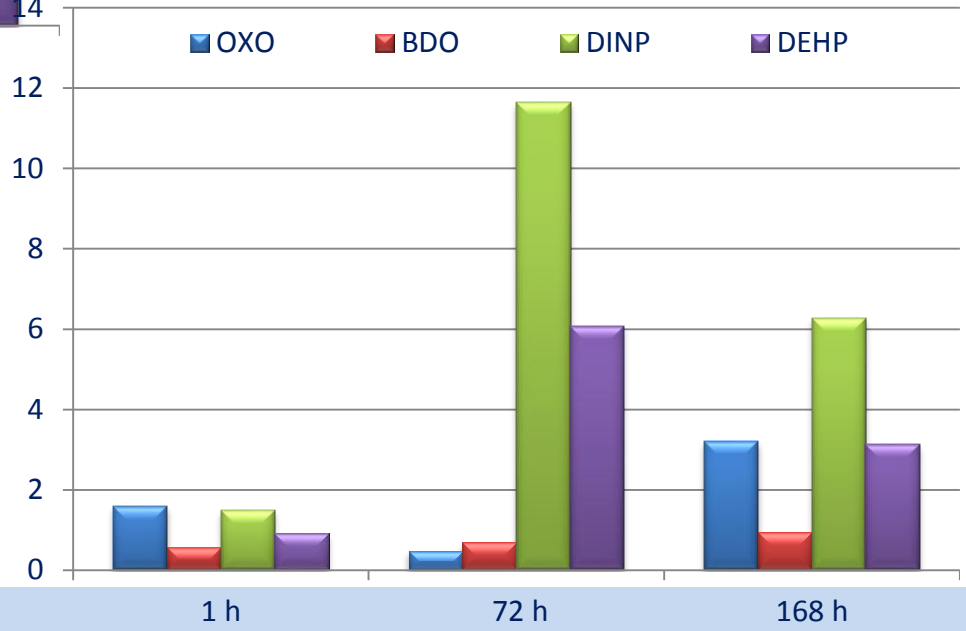
Change in viscosity in time for pastes containing 50 parts of plasticiser [Pas]

Results of tests on pastes

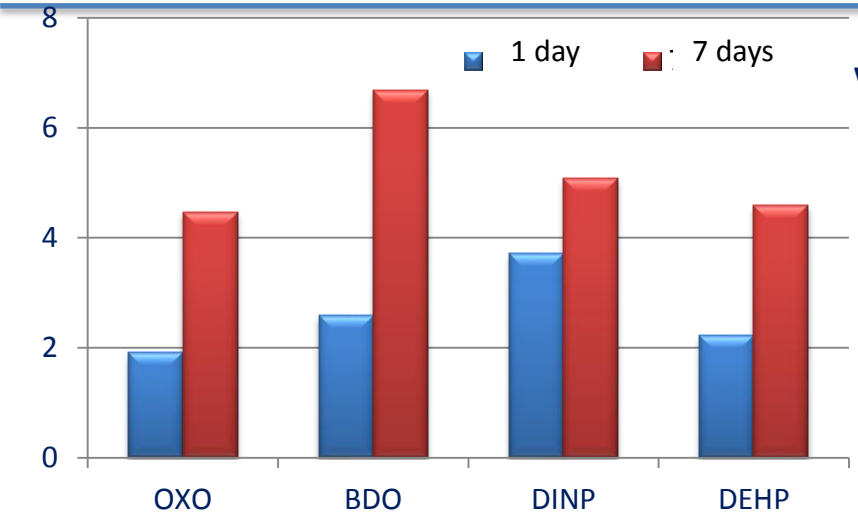


Change in viscosity in time for pastes containing 70 parts of plasticiser [Pas]

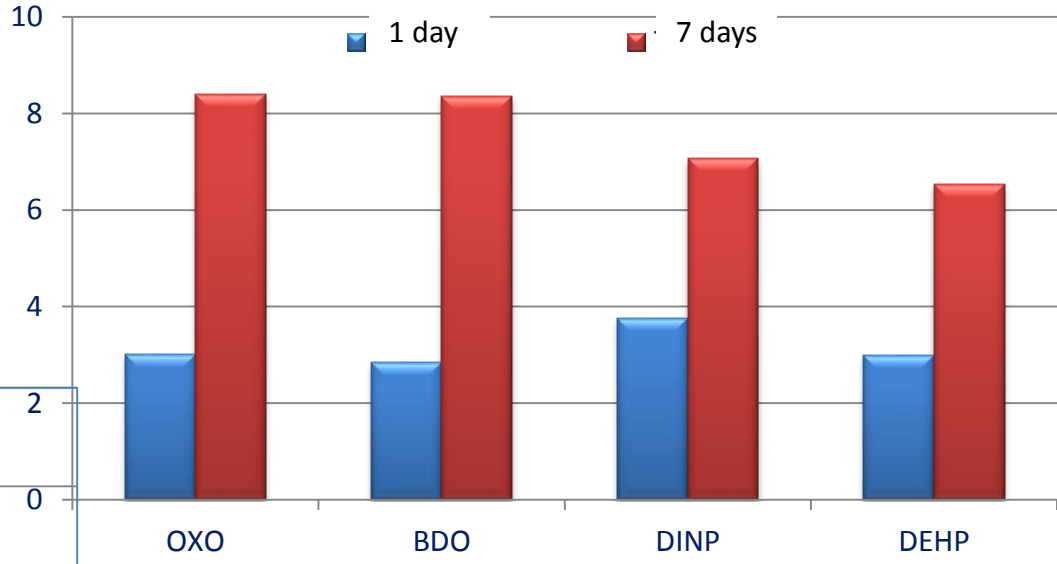
Change in viscosity in time for pastes containing 90 parts of plasticiser [Pas]



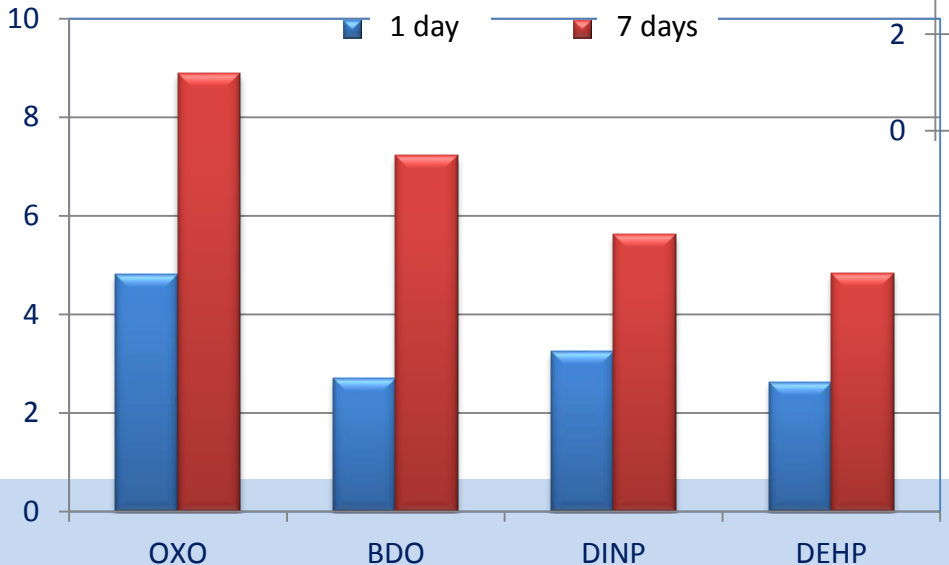
Results of tests on pastes



water absorption of coatings containing
50 parts of plasticiser [%]

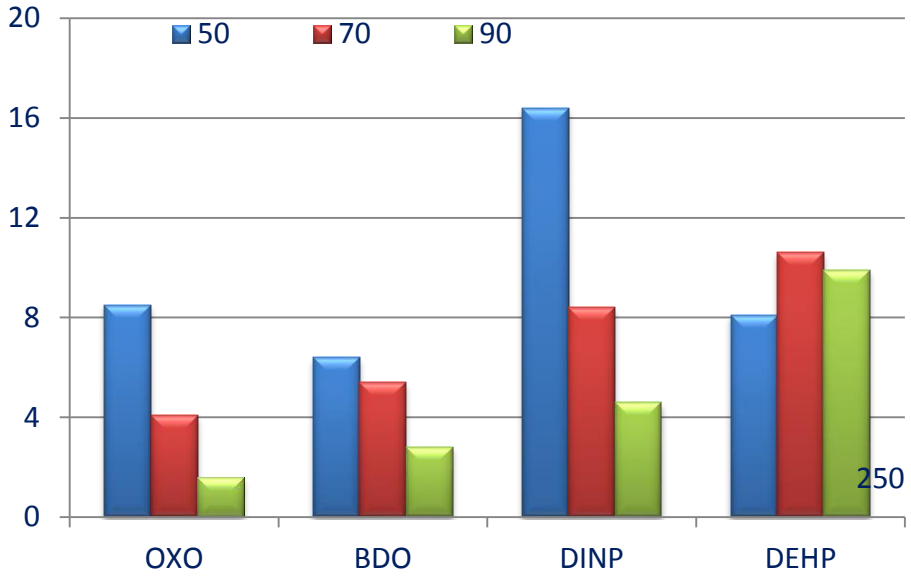


water absorption of coatings containing
70 parts of plasticiser [%]



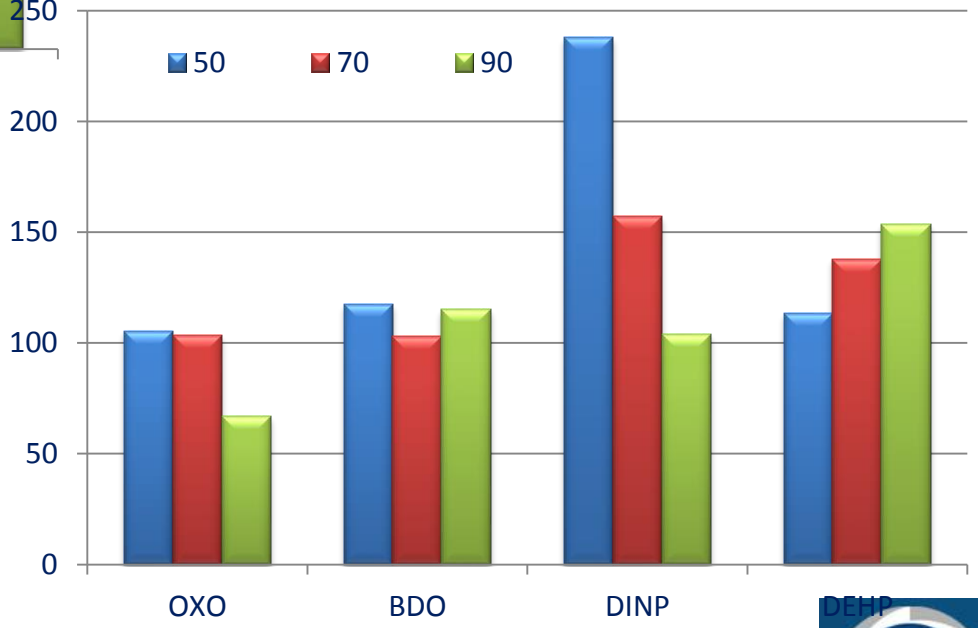
water absorption of coatings containing
90 parts of plasticiser [%]

Results of tests on pastes



Tensile strength of the tested pastes with varying content of plasticiser [MPa]

Relative elongation at break of the tested pastes with varying content of plasticiser [%]



Directions for the use of new types of plasticisers

PVC-P products:

-– calandered products: films, boards, sheet flooring
-– extruded products: hoses, gaskets, pipes
-– polwiplast products for sports footwear soles
-– stretchy films

Plastisols:

-– coated fabrics, artificial leather
-– metal coating

Other:

-– adhesives
-– latex seals

Conclusion

- Restrictions and regulations on the safe use present a challenge to the chemical industry and processors of plastics of finding replacements capable of fully substituting for phthalates both technically and economically.
- Non-phthalate plasticisers have been developed for demanding applications in products such as medical equipment, toys, food packaging, etc. and are currently more and more often used for general applications.
- A large variety of types of plasticisers and their functionality leads to higher and higher expectations in relation to the product properties obtained thanks to them.
- Alternative plasticisers replacing phthalates are often more expensive but the PVC industry takes action to use it because of REACH.

The fact is that PVC is a plastic polymer that is universal, affordable and not likely to be replaced in the near future, ***therefore studies should first of all focus on the synthesis of high-performance plasticisers capable of fully substituting phthalates that have turned out to be toxic.*** *Studies are being conducted to improve their properties and softening effectiveness.*

Literature

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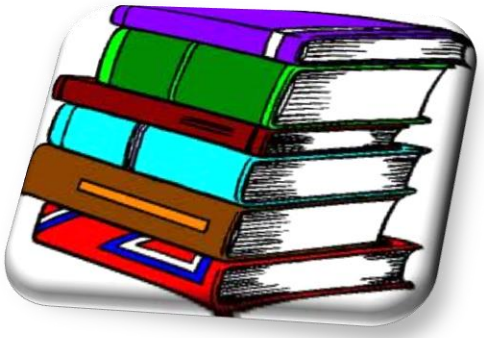

Thank you