Flexidone™ – A New Class of Innovative PVC Plasticizers

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1. Introduction

It has been found, that N-alkyl-(C8 to C18) pyrrolidones are highly efficient, strong solvating performance plasticizers which decrease gelling temperatures substantially (Bonnet & Kaytan, 2008). They facilitate fast gelling, produce flexibility at extremely low temperatures. Higher alkyl pyrrolidones also exhibit very low volatility. After these excellent properties were proven by industrial trials in several different applications such as flooring, gloves, window sealing and wires, they were introduced to the market as Flexidone plasticizers.

Solubility temperatures of the N-alkyl-pyrrolidones (DIN 53408) are between 52° C (N-octyl-pyrrolidone) and 80° C (N-octadecyl-pyrrolidone). Accordingly, the gelling temperatures are substantially lower than with the standard plasticizers.

Plasticizing efficiency of the different Flexidone Types were tested through comparative determination of Shore A values. It could be shown that Flexidones are about 30-50% more efficient than the standard plasticizer DINP (diisononyl phthalate).

Cold Flexibility with the Flexidones was checked by the Folding test DIN EN 495-5.

Further trials in filled systems showed that Flexidones are highly compatible with e.g. calcium carbonate and allow very high filler loads with outstanding mechanical properties. Manufacturing tests with a highly filled system using an extruder resulted in increased output while significantly reducing plasticizer levels and processing temperatures.

In the broader effort to offer to the flexible-PVC industry cost-effective plasticizer systems with desired process- and end product properties, tests were performed on blends with various low cost secondary plasticisers. In these experiments, all Flexidone types have worked as performance boosters and compatibilizers.

Exemplarily the results of blends with certain fatty acid esters and chlorinated types will be presented. As a function of the ratio of mixture indentation hardness, tensile properties and gelling properties (plastisol) have been evaluated.

Compared to common systems, these new Flexidone mixtures surpass the performance characteristics and are superior to most of the phthalate and phthalate free systems. All of

the products are now industrially produced REACH-compliant types that are globally available in appropriate volumes.

2. Properties of Flexidones in soft-PVC applications

In terms of worldwide consumption polyvinyl chloride (PVC) stands in third place behind polyethylene (PE) and polypropylene (PP). Thank to the development of a wide range of functional additives, in particular thank to effective plasticizers PVC could achieve this important commercial relevance. PVC is one of the few thermoplastics whose hardness can be adjusted from rubber-like elasticity up to hard formulations (Franck & Knoblauch, 2005). Thus for well over 50 years plasticizers have been playing a significant role in the manufacture of soft PVC products for the most versatile applications from floor coverings to roof membranes, cable insulation to blood bags.

With a market share of approximately 85 % phthalate plasticizers — di-2-ethyl hexyl phthalate (DEHP), diisononyl phthalate (DINP) and diisodecyl phthalate (DIDP) — represent the most significant class of plasticizers at present. They are the all-rounders amongst plasticizers. The remaining 15 % are taken up by plasticizers that show excellent properties in particular areas even if they have weaknesses in others. For instance trimellittic acid esters exhibit particularly good heat stability, whilst phosphoric acid esters confer fire resistance. Polymeric plasticizers (polyesters) come into play when excellent oil resistance and very good migration behaviour is required.

However, for more than 25 years, plasticizers in particular phthalates, have been the subject of environmental and health debate despite attempts by the industry to defend their current status with ever new data. This has however initiated the development of numerous new plasticizers as phthalate substitutes with less toxicological concern. One of the best known examples of these new plasticizers is Hexamoll DINCH (1.2-cyclohexanedicarboxylic acid diisononyl ester) which was developed by BASF for sensitive applications.

Unfortunately most of the newly developed plasticizer alternatives do hardly offer any improvements in the processing behaviour or property profile of soft PVC alongside the ecological or toxicological factors.

Now, however, ISP-Ashland Specialty Ingredients, Cologne, Germany, and the Institute for Materials Technology at the University of Applied Sciences Cologne (Institut für Werkstoffanwendung der Fachhochschule Köln) have collaborated to develop a new class of plasticizers for PVC based on linear alkyl pyrrolidones. Initial results show that they are not only free from physiological concerns – e.g. acute toxicity is relatively low, dependent on alkyl chain length so that the LD $_{50}$ for example lies between 2.05 g/kg for Flexidone 100 (C-8 Pyrrolidone) and >12 g/kg for Flexidone 500 (C-16/18 Pyrrolidone) (Ansell & Fowler, 1988) –, but also possess several outstanding properties. These properties enable gentler, cost saving processing of soft PVC and make it possible to produce highly flexible products for low temperature applications.

2.1 Structure and mode of action

Due to the planar structure of pyrrolidones the oxygen with its high electronegativity can easily cause an electron to delocalize (Fig. 1). This produces a strong dipole moment.

Chemically binding a flexible non-polar alkyl chain with a compact hydrophilic head makes the alkyl pyrrolidones soluble in both polar and non-polar solvents. Even though the alkyl chain length can be adjusted to lie between C4 and C30 it has been found that chain lengths between C8 and C18 are particularly suitable for use as plasticizers. Due to their excellent dissolving power and good compatibility with PVC both gelling temperature (very low solubility temperatures – see Fig. 2) and gelling time (see gelling curves Fig. 9 and 14) can be substantially reduced. At the same time this leads to highly flexible PVC formulations that do not lose their flexibility even at extremely low temperatures.

Fig. 1. Electron delocalization in pyrrolidones.

2.2 More cost effective dry blending

A measure of the effectiveness of a plasticizer is its solubility temperature. This is the temperature at which a plasticizer completely dissolves a given PVC. Typical solubility temperatures lie between 87°C for butyl benzyl phthalate and 151°C for DINCH, with disononyl phthalate at 129°C. Figure 2 shows the solubility temperatures for alkyl pyrrolidones with various alkyl chain lengths. It can be seen that the solubility temperature can be adjusted by chain length to lie between 52 and 80°C and is thus significantly lower than the solubility temperatures of conventional plasticizers.

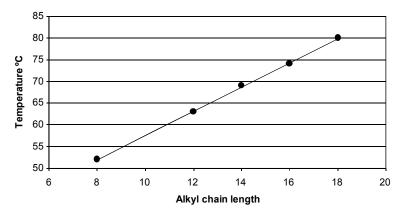


Fig. 2. The dependence of solubility temperature of various alkyl pyrrolidones on alkyl chain length in accordance with DIN 53 408.

This also reduces the time taken to produce a dry blend in a high speed cooler mixer without the need for external heating. Depending on the formulation mixing times can be reduced down to 20 % in comparison to phthalate plasticizer formulations. In addition,

processing temperatures are lowered by 20 to 40°C in comparison to classic soft PVC processing. These significantly lower temperatures allow the use of temperature sensitive additives such as special colorants and scents and result in clear time and cost savings through the use of alkyl pyrrolidone plasticizers in comparison to standard plasticizers.

2.3 Cold break at temperatures lower than -70°C

The efficiency of the plasticizing effect of the Flexidones can be seen very clearly in comparative measurements of hardness (Shore A) in relation to the plasticizer content with DINP as the standard plasticizer (Fig. 3). These show e.g. a hardness of 80 Shore A can be achieved with 33 parts of Flexidone 300 (C-12 Pyrrolidone) compared to 60 parts of DINP. In this example the same flexibility can be reached with 45 % less plasticizer.

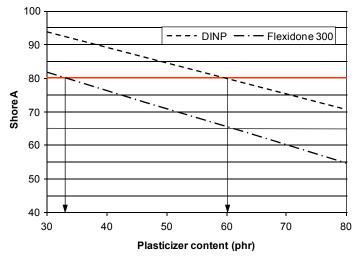


Fig. 3. The dependence of hardness on plasticizer content (parts per100 parts of PVC) tor DINP and Flexidone 300.

The hardness is determined at room temperature, however, in many applications the temperature can be temporarily or permanently significantly lower. Many soft PVC formulations are not only much harder at lower temperatures but also completely lose their toughness so that they are subject to brittle fracture under flexural or tensile loadings. A practical test for determining this boundary temperature is DIN EN 495-5 (foldability at low temperature). However, since it is not only the plasticizer type and concentration that is responsible for low temperature behaviour, but also the molecular weight of the PVC grade used, tests were performed with two different concentrations (40 and 60 parts) of Flexidone 300, Flexidone 500 and DINP in PVC grades with K-values of 60, 70, 80 and 99 (Fig. 4). This showed that the cold break temperature could be reduced by 15 to 30°C through the use of Flexidones. At 60 parts of Flexidone 300 and 500 the exact cold break temperature could not be determined for the higher K-values since the cooling system of the tests apparatus could only produce temperatures down to -70°C and at this temperature none of the samples with each 60phr Flexidone 300 and 500 showed breakages or cracks. Flexidone 500 is therefore

the first available low volatility plasticizer which could facilitate cold break temperatures of lower than -70°C.

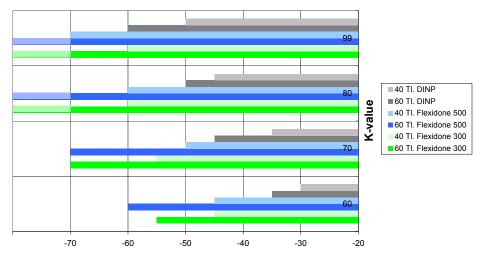


Fig. 4. Determination of the low temperature break behaviour according to DIN EN 495-5 (foldability at low temperatures) for soft PVC sheets with various concentrations of Flexidone 300, Flexidone 500 and DINP for a range of PVC grades with different K-values.

Figure 5 shows the progression in Shore A hardness at temperatures between +20°C and -50°C for Flexidone 300, Flexidone 500 and DINP as well as DOA which is a widely used low temperature plasticizer. It is very noticeable that Flexidone grades not only have a better

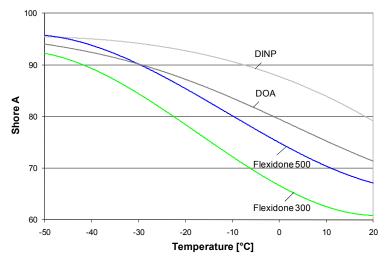


Fig. 5. Variation of Shore A values at temperatures between +20°C and -50°C for samples with 60 parts of Flexidone 300, 500, DOA (dioctyl adipate) and DINP.

plasticizing power in comparison to DINP and DOA at room temperature, but the progression in hardness with decreasing temperature is also very different, i.e. an initially even gradient is followed by a sharper rise. This means that Flexidones show significantly higher cold flexibility than conventional plasticizers at temperatures in the region of -20 °C which are typical for exterior applications. Thus the use of Flexidone grades not only enable extremely low cold break temperatures, but also delivers soft PVC with significantly better flexibility at very low temperatures.

2.4 Good mechanical properties

As Figures 6 and 7 show the mechanical properties of soft PVC film made with Flexidone 500, particularly at higher K-values, have comparable mechanical values to samples made with the same content of DINP. This is remarkable considering that these samples are significantly softer whilst as shown earlier also retaining their flexibility down to the very low temperatures.

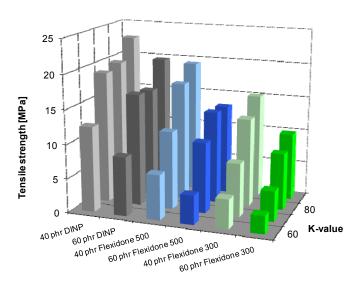


Fig. 6. Tensile strength of flexible PVC sheets with various concentrations of Flexidone 300, Flexidone 500 and DINP in PVC grades with different K-values.

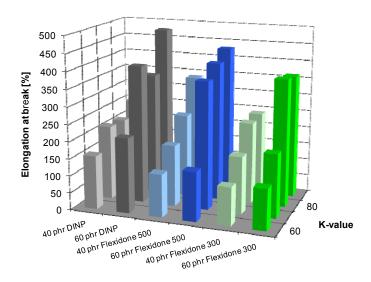


Fig. 7. Elongation at break for soft PVC sheets with various concentrations of Flexidone 300, Flexidone 500 and DINP in PVC of different K-values.

2.5 Properties of highly filled systems

Fillers are used in plasticized PVC to reduce costs, and also to facilitate a special change in properties so that the compound largely meets the requirements of the end products (Hohenberger, 2001). Among the fillers, calcium carbonate, with a worldwide market share of approximately 70%, plays the dominant role. For plasticized PVC, depending on the application (cable, floor covering, profiles, films), uncoated or coated calcium carbonate grades, with different particle sizes, can be used. For all experiments a stearic acid coated calcium carbonate with a d50% value of 2.4 μm and a top cut of 20 μm (Omya BSH) was used.

In highly filled systems, e.g. with a calcium carbonate content of 150 phr important mechanical properties, like the tensile strength, can easily drop down to less than 50%, compared to the unfilled systems if a standard plasticizer like DINP is used. For a highly filled system with Flexidone 300 as plasticizer, all essential mechanical properties vary only insignificantly from the unfilled system. As shown in Figure 8, softness of the Flexidone 300 formulation decreases only slightly in comparison to DINP even with a filler load of 100 phr Calcium carbonate.

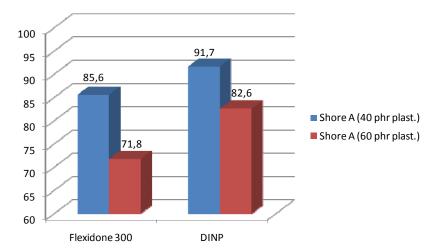


Fig. 8. Shore A-values with Flexidone 300 and DINP, each filled with 100 phr CaCO₃.

Therefore the formulation costs can be lowered in many applications using Flexidones with remarkably increased filler loads.

2.6 Improvements in plastisol production

Plastisols take a special place in processing of PVC since they are moulded as liquids or pastes rather than in a thermoplastic state. The solidification, the so called gelling, takes place at the end of molding through heat treatment at 120 to 200°C (Franck & Knoblauch, 2005).

In making these pastes the processing behaviour can be significantly improved in many respects by the substitution of around 10% of the plasticizer with Flexidone 100 (octyl pyrrolidone). Degassing at the end of mixing and homogenizing the plastisol mixture is intended to minimize defects in the subsequent processing of the pastes. Flexidone 100 is amongst the surfactants with the highest dynamic wetting properties. This means that a partial substitution is sufficient in order to reduce foaming to a minimum and thereby significantly shorten degassing cycles.

During the processing of PVC plastisols the gelling temperature is of particular interest. Therefore substantial efforts have been made in order to lower the gelling temperature. It is determined via measurements of the complex viscosity against temperature. After an initial drop once gelling begins there is a rise in the viscosity of more than four orders of magnitude. The gelling temperature is the point of inflection on the curve. Figure 9 shows viscosity measurements of plastisols with 50 parts Vestinol 9 (DINP) and plastisols, in which 1, 3, 5 and 10 parts of Vestinol 9 were replaced by Flexidone 100. Due to the significantly higher dissolving power of Flexidone 100 the gelling temperature can be significantly reduced. Each part of Flexidone 100 causes approximately 2°C drop so that a blend of Vestinol 9/Flexidone 100 at a ratio of 40/10 reduces the gel temperature by 20°C. The viscosity profile is at the same time not affected at all and only after storage for a long time a small increase in viscosity could be seen.

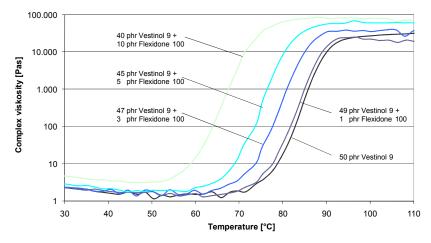


Fig. 9. Gelling curves of PVC plastisols (50 phr plasticizer) with various mixtures of Vestinol 9 (registered trade mark of Evonik for DINP)/Flexidone100.

Comparable results were also found for blends with Hexamoll DINCH, but the initial viscosities were much lower and the viscosity after prolonged storage rose insignificantly.

3. Mixed plasticizer systems

Through these outstanding processing and physical properties and the extremely high compatibility, Flexidones enhance the tolerance level of low cost secondary plasticizers in PVC so that these could be used in very high amounts. Adding Flexidone 300 or 500 to secondary plasticizers like fatty acid esters, chlorinated Paraffines/esters, ESO (epoxidized soybean oil) as well as to primary plasticizers like DOA

decreases the

- indentation hardness
- cold flexibility temperature
- processing temperature
- processing time

and increases the

- compatibility
- gelling speed
- clarity / transparency.

3.1 Flexidone-fatty acid ester-system

In figure 10 and 11 the effect of Flexidone 300 and 500 on the tensile strength and elongation at break in mixtures with a fatty acid ester can be seen. All mixtures have a total plasticizer content of 60 phr. The results prove the excellent compatibility of this system with good mechanical properties in all concentrations up to 75% fatty acid ester.

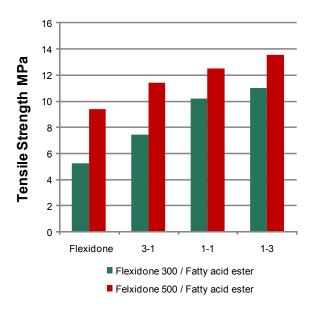


Fig. 10. Tensile strength for Flexidone 300 and Flexidone 500 in mixtures with a fatty acid ester.

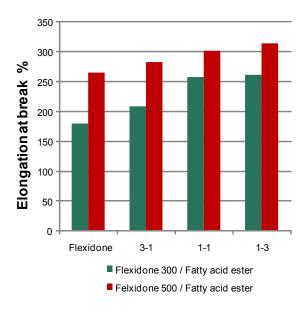


Fig. 11. Elongation at break for Flexidone 300 and Flexidone 500 in mixtures with a fatty acid ester.

As it can be seen in figure 12 the hardness increases with increasing fatty acid ester content. But all examined mixtures show still higher plasticizing efficiency than DINP.

Most interestingly all mixtures with a ratio between 3:1 and 1:3 show cold foldability temperatures of -70°C and below! Therefore the costs can be reduced by mixing Flexidone's with fatty acid esters while improving tensile properties and still benefit from excellent cold flexibility.

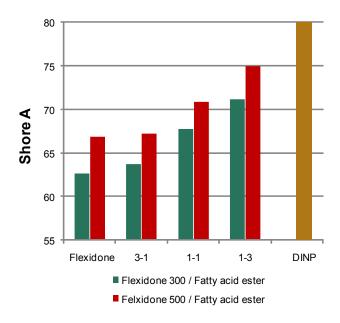


Fig. 12. Indentation hardness for Flexidone 300 and Flexidone 500 in mixtures with a fatty acid ester in comparison to DINP.

As a conclusion of these results ISP commercialized different Flexidone / fatty acid ester - blends such as Flexidone 350FE, Flexidone 333FE, Flexidone 550FE and Flexidone 533FE. Flexidone FE yields stable, low-viscosity plastisols with excellent shelf life and desirable fast-fusing properties. This combination enables the system to be used in various production methods such as extrusion, calendaring and injection molding. Additionally they provide low-viscosity plastisols with good gelling properties. As figure 13 indicates, of various samples of plastisol formulations, those with Flexidone 333FE and 533FE exhibit the best viscosity stability after 28 days, enlarging the processing window for many product manufacturers.

In addition to better viscosity stability, Flexidone FE improves the gelling behaviour of PVC products, which affects its strength. In figure 14, the gelling rates of Flexidone 333FE and 350FE were the fastest compared with other Flexidone grades and a DINP.

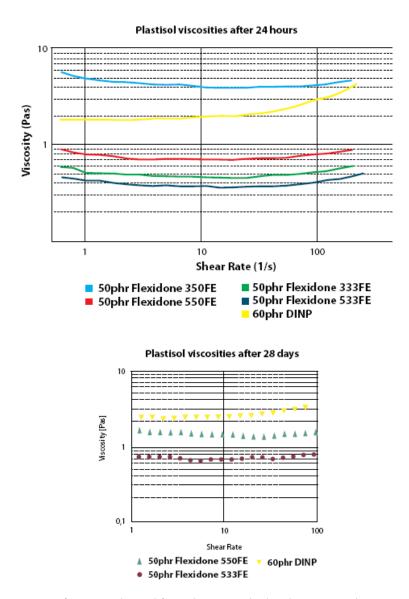


Fig. 13. Viscosity of various plastisol formulations with Flexidone FE Grades compared with DINP.

The Flexidone FE grades behaviour in plastisol can be summed up as:

 Flexidone 350FE offers fast and low-temperature gelling, improved transparency and homogeneity. As a primary plasticizer for plastisols (for immediate processing), it is an extremely fast fusing system requiring about 30% less use than standard plasticizers.

- Flexidone 333FE can be used as primary plasticizer; about 15% more efficient than other systems; has lower plastisol viscosity than 350FE and stays stable even after longer storage.
- Flexidone 550FE can be used as primary plasticizer with gelling properties similar to 333FE but at a lower viscosity with higher clarity and lower volatility.
- Flexidone 533FE for very-low-viscosity plastisols; can also be stored for very long time.
 Lower volatile.

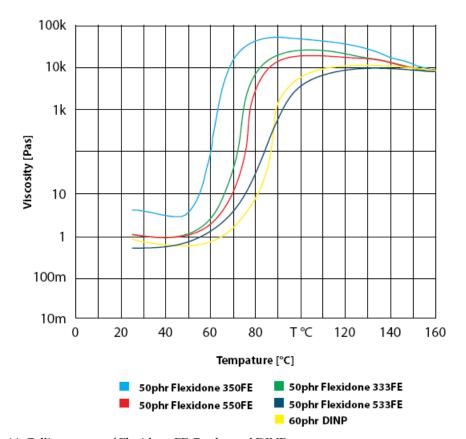


Fig. 14. Gelling curves of Flexidone FE Grades and DINP.

3.2 Flexidone-chlorinated ester-system

Similar experiments as with the Flexidone/fatty acid ester-systems were performed for the plasticizer systems Flexidone/chlorinated ester. In figure 15 and 16 the effect of Flexidone 300 and 500 on the tensile strength and elongation at break in mixtures with a Cl-ester can be seen. All mixtures have a total plasticizer content of 60 phr.

The results prove the superior compatibility of this system with good mechanical properties in all concentrations up to 75% Cl-ester. Especially the 1:1-mixture with Flexidone results in

a rubber like behaviour with elongation at break values of over 500%. From this 500% elongation over 450% is elastic deformation and less than 50% is plastic deformation.

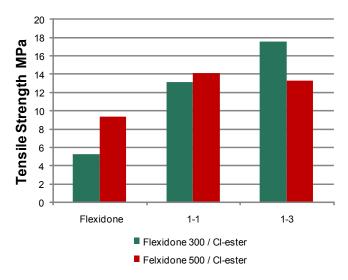


Fig. 15. Tensile strength for Flexidone 300 and Flexidone 500 in mixtures with a Cl-ester.

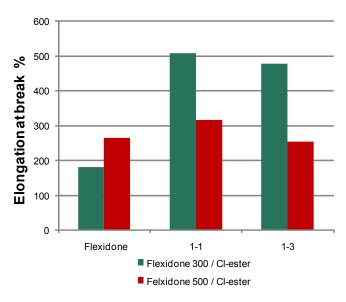


Fig. 16. Elongation at break for Flexidone 300 and Flexidone 500 in mixtures with a Cl-ester.

Although the plasticizing efficiency reduces with increasing Cl-ester content, even Flexidone/Cl-ester-mixtures with very high Cl-ester content show Shore A values similar to a sample with the same amount of DINP (see figure 17).

Analogue to the indentation hardness results the cold flexibility in the mixtures with Clester is slightly inferior to the corresponding Flexidone/fatty acid ester system. Still all measured samples show cold foldability temperatures of -40°C and below.

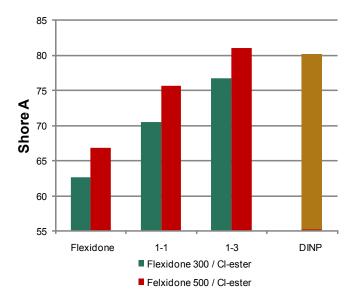


Fig. 17. Indentation hardness for Flexidone 300 and Flexidone 500 in mixtures with a Clester in comparison to DINP.

4. Product developments

Over the last few years a significant number of product trials have been performed to test Flexidone in existing formulations or in new product developments successfully.

4.1 Shoe soles

Shoe soles are just one example for various soft-PVC applications ISP was asked to come up with alternative formulations. Following two formulations will be presented here:

- one formulation with 80 phr DINP, 40 phr chlorine paraffin and 20 phr CaCO₃ and
- one formulation with 80 phr DOA.

As a substitute for the DINP/CP-system (with Shore A 53) we could offer a Flexidone/ESO system with 80 phr ESO and 20 phr Flexidone 300 showing the same softness (Shore A 50) and lower processing temperature even with a lower plasticizer content and an increased amount of CaCO₃ (see Table 1).

PVC	100	100
DINP	80	-
СР	40	-
Flexidone 300	-	20
ESO	5	80
Plasticizer total	125	100
CaCO ₃	20	50
Stabilizer	2,5	2,5
Shore A	53	50

Table 1. Formulation and Shore A for soft-PVC shoe soles containing Cl-paraffin.

In case of the DOA system the aim was to improve the softness from Shore A 60 to 56, at the same time increasing of the compatibility/processability of DOA and improving the clarity. The target could be achieved by replacing 20 phr DOA with the same amount of Flexidone 300 (see Table 2).

PVC	100	100
DOA	80	60
Flexidone 300	-	20
ESO	5	5
Stabilizer	2,5	2,5
Shore A	60	56

Table 2. Formulations and Shore A for soft-PVC shoe soles with reduced Hardness.

These two examples show what a powerful tool Flexidone is in solving a lot of practical processing and/or performance problems of flexible PVC formulators. An extensive set of experimental data is available to help finding solutions to meet customers' needs.

4.2 Avoiding use of critical plasticizers

In studies of rodents exposed to certain phthalates, high doses have been shown to change hormone levels and cause birth defects (National report, 2009). Therefore in the U.S. children's toy or child care article that contains concentrations of more than 0.1 percent of DEHP, DBP (dibutyl phthalate), or BBP (butylbenzyl phthalate) are illegal (Congress, 2007). In plastisol applications DBP and BBP are widely used as fast-fusing plasticizers in DINP. As figure 18 proves, Flexidone 100 and 300 can easily replace fast-fusers with unfavourable ESH profile.

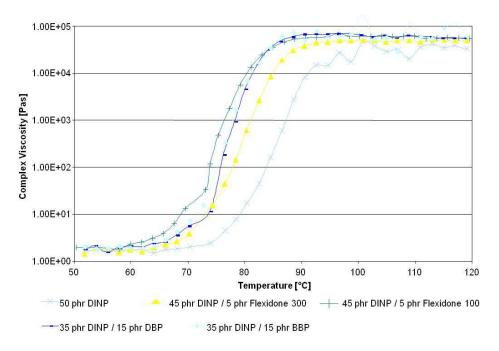


Fig. 18. Gelling curves of PVC plastisols (50 phr plasticizer) with various mixtures of Vestinol 9 and Flexidone100, 300, DBP and BBP.

5. Conclusion

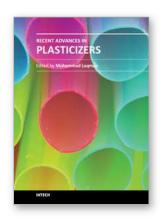
It could be shown, that Flexidone's are very efficient PVC plasticizers. They are up to 50% more efficient than standard plasticizer. Since they improve a lot of mechanical and processing properties in mixed plasticizer systems, cost effective plasticizer systems with superior properties could be presented. In any case the presence of Flexidone in the plasticizer system results in

- lower plasticizer use (⇒ easier processing and less migration)
- lower gelling temperatures (⇒ energy saving)
- faster gelling (⇒ higher production rates)
- better cold flexibility (⇒ more durable products at low temperatures)
- better compatibility (⇒ higher transparency and homogeneity as well as more fillers and use of less compatible materials)

Therefore the Flexidone family of plasticizers represents breakthrough technology in "cold flex" performance of plastics. Depending on the application, it can offer a great deal more. Flexidone plasticizers expand the options in PVC formulation, manufacturing and end-product design. This flexibility lets re-imagine the potential of demanding applications and reconfigure processing for unprecedented efficiencies.

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Recent Advances in Plasticizers

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Plasticizers are used to increase the process-ability, flexibility, and durability of the material, and of course to reduce the cost in many cases. This edition covers introduction and applications of various types of plasticizers including those based on non-toxic and highly effective pyrrolidones, and a new source of Collagen based bioplasticizers that can be obtained from discarded materials from a natural source; Jumbo Squid (Dosidicus gigas). It covers the application of plasticizers in plastic, ion-selective electrode/electrochemical sensor, transdermal drug delivery system, pharmaceutical and environmental sectors. This book can be used as an important reference by graduate students, and researchers, scientists, engineers and industrialists in polymer, electrochemical, pharmaceutical and environmental industries.

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