# Benchmark for Plasticizers

## *Phthalate-Free Plasticizer for Flexible PVC on the Test Stand*

The properties of polyvinyl chloride are adjusted using plasticizers for many applications. Phthalate-free plasticizers can keep pace here with conventional versions containing phthalates in many technical fields. This article demonstrates that based on a comparative study.

Soft PVC is used in many sports and leisure products. The plasticizer used in these applications should be firmly bonded in the polymer matrix, with no migration (© 123RF.com/nazdravie)

Plasticizers modify the hardness and brittleness of polyvinyl chloride (PVC). Thus, the mechanical properties of soft PVC formulations can be adjusted. They also have a major influence on the lifespan of the materials. Low-molecular phthalate plasticizers generally make PVC softer, cause it to gel better, and are absorbed more readily. They are, however, more volatile as well, which is a concern in regards to their stability, safety, and sustainability. High-molecular, phthalate-free plasticizers on the other hand are less volatile, therefore have a lesser migration tendency, and last longer. They are, however, not as efficient in yielding softness, and they gel more slowly. With these characteristics, compromises always had to be made so far for soft PCV formulations. This article compares the behavior and characteristics of phthalate-free alternatives.

Three phthalate-free softeners were tested:

- PETV (pentaerythritol tetravalerate) from Perstorp Holding AB, Malmö, Sweden, marketed as Pevalen,
- DINCH (1,2-cyclohexane dicarboxylic acid diisononyl ester) from BASF SE, Ludwigshafen, Germany, marketed as Hexamoll,
- DOTP (dioctyl terephthalate, a terephthalate considered a non-phthalate by some because it is assumed that the safety concerns apply only to isophthalates and orthophthalates).

A plastisol base formulation (**Table 1**) was used to test six criteria that are relevant for the processing and application of the PVC plastisol. All mixtures consisted respectively of 100 phr PVC and 50 phr plas-

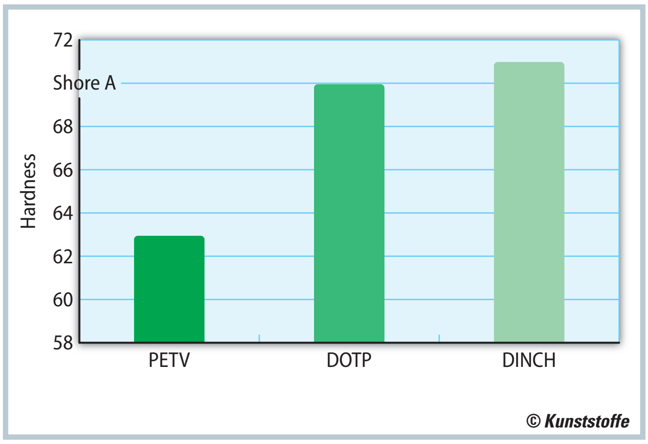


**Fig. 1.** The comparison of the shore A hardness shows that PETV is most efficient compared to the other test candidates (source: Perstorp)

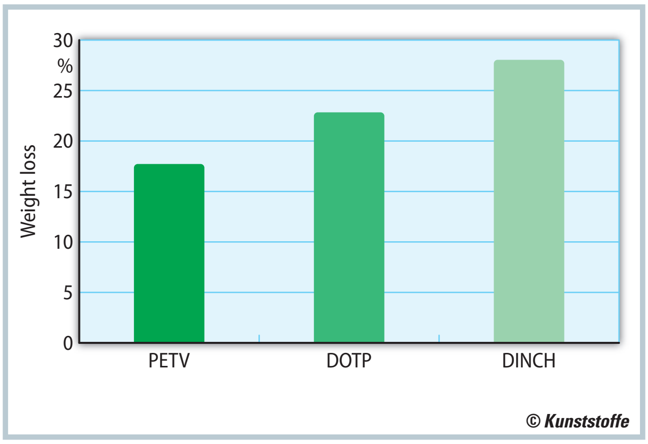


**Fig. 2.** Volatility of the softeners. Since the additives have a significant influence on the characteristics of PVC, their amount should remain constant during the entire lifespan of the material (source: Perstorp)

ticizer. The test results that follow describe the technical characteristics of the three phthalate-free plasticizers .

## *Hardness and Volatility*

As mentioned at the outset, adjusting the hardness with plasticizers is very important for soft PVC, especially when the material is used in coated textiles. The lesser amount used and still softer PVC, the more efficient is the plasticizer . Reduced raw material input can lower costs since the mixing ratio of softener to PVC is 50:50 in some formulations. Low raw material consumption also has a positive impact on the environmental profile.

All three non-phthalates fared very well in the hardness test, with a better softening effect compared to similar benchmark tests with phthalates (**Fig. 1**). In general one can say that the lower the value, the more effective, and the softer the PVC material is. PETV was more than 15 % softer than DINCH and more than 10 % softer than DOTP. In regards to this point, PETV is superior to all leading phthalate-free and phthalate-containing softeners.

The volatility of the softener is important since both weight loss and migration are reduced if this value is low. It also allows the PVC plastisol to retain its stability and shape over the entire period of use. Furthermore, the softeners are responsible to a large extent for the characteristics of the PVC, and therefore should not migrate. The larger the molecular mass, the lower the risk of migration or extraction due to material contact or solvents such as water. The molecular mass of the three non-phthalates in the test was as follows:

- PETV: 472 g/mol,
- DINCH: 425 g/mol,
- DOTP: 391 g/mol.

The volatility is measured according to the loss of weight during a period of 7 days at 100 °C. In this test, PETV had the lowest volatility with a weight loss of 17.5 % compared to DOTP (22.5 %) and DINCH (26 %) (**Fig. 2**).

## *Fogging Behavior and Viscosity*

The fogging behavior, which describes the outgassing of volatile compounds on glass panes and windshields, is directly related to the volatility. PVC materials and films frequently release volatile substances when exposed to heat or warm indoor temperatures, for example in the car. Reduced fogging values improve the visibility for drivers, especially when the sun is low in the sky and at night. In the fogging test, the reflectometer value is deter- »

| Ingredients | Phr |
|---|---|
| PVC K-70 | 100 |
| Plasticizer | 50 |
| Epoxydized soy oil (ESBO) | 2–5 |
| Stabilizer* | 2–3.5 |

*Recommended stabilizers: Baerostab 711-1 X RF, Lankrostab LZB 864, Naftosafe P XX 30152 OBS + Naftolube HRP 83683, Reagens CLX 759-9-SF

**Table 1.** The initial formulation of the plastisol in which each of the three plasticizers was tested (source: Perstorp)

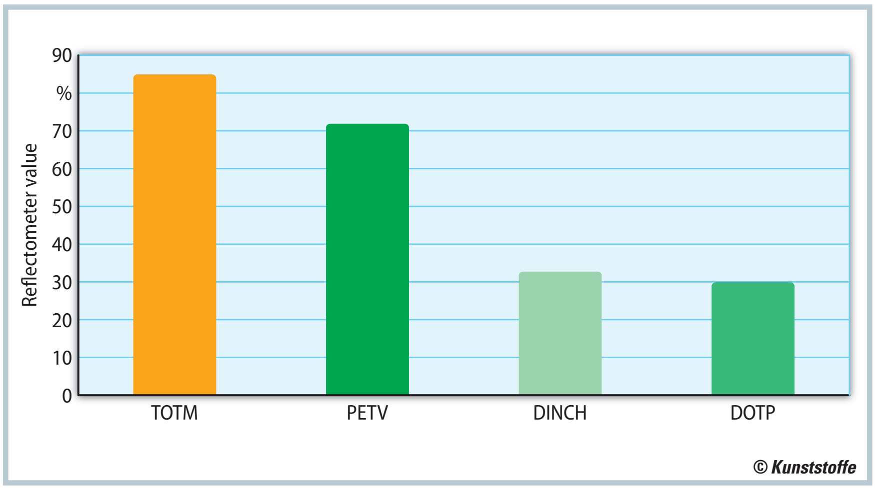


**Fig. 3.** Fogging test according to DIN 75201-A on an automotive film (700 g/m², 75 phr). The reflectometer value was determined on a glass plate. Here the phthalate-free plasticizer trioctyl trimellitate (TOTM) was tested in addition (source: Perstorp)

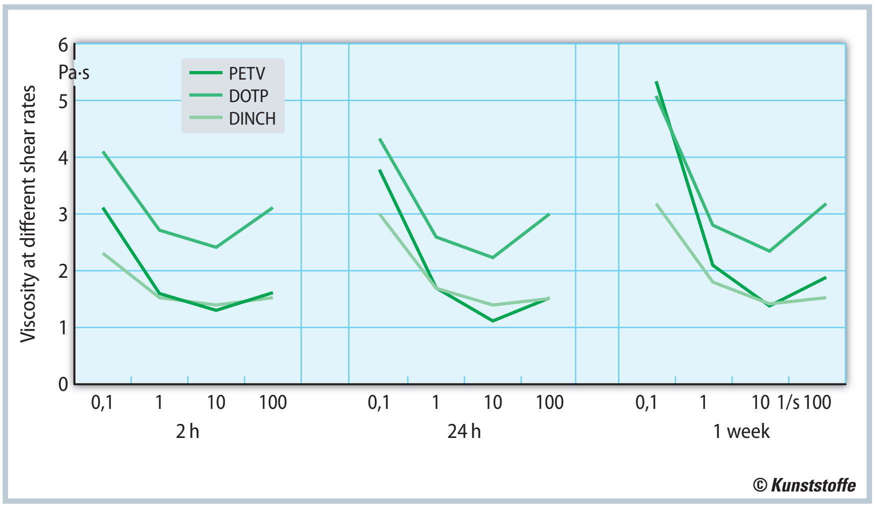


**Fig. 4.** The viscosity comparison shows that the softener DINCH keeps the plastisol constant over a long period of time, and is therefore well suited for delayed processing (source: Perstorp)

mined on a glass plate after a corresponding automotive film has been exposed to high heat (**Fig. 3**). This test proves that PETV loses considerably less weight and also has a higher reflectometer value.

A low initial viscosity is required for the processing of PVC to ensure it exhibits uniform flow characteristics in the manufacturing process. This applies in particular to plastisols where several days may elapse between production and processing. The viscosity has to remain low when time delays occur between mixing and processing. Only then can unnecessary manufacturing costs or time delays be avoided. DINCH obtained excellent results in this test, both in terms of the initial viscosity and over a longer period of time, closely followed by PETV (**Fig. 4**). Both plasticizers are well suited for plastisols that are not processed until several days after their production. They maintain their low viscosity during this period.

## *Polymerization and Processing*

Gelling and absorption of the plasticizer in PVC are important for the production of large flexible PVC articles. The faster the liquid substances used become solid plastic, the shorter the processing time. This has a positive impact on the productivity and quantity. The degree of processing is specified as a strain value and is a function

| Time [min] | Temperature [C°] | Plasticizer | Elongation [%] |
|---|---|---|---|
| 2 | 160 | PETV<br>DINCH | 100<br>70 |
| 5 | 160 | PETV<br>DINCH | 300<br>100 |
| 3.5 | 180 | PETV<br>DINCH | 415<br>295 |
| 2 | 200 | PETV<br>DINCH | 470<br>280 |
| 160 | 160 | PETV<br>DINCH | 400<br>430 |

**Table 2.** Processing temperature and time in which the plasticized PVC respectively reach the desired degree of elongation (source: Perstorp)

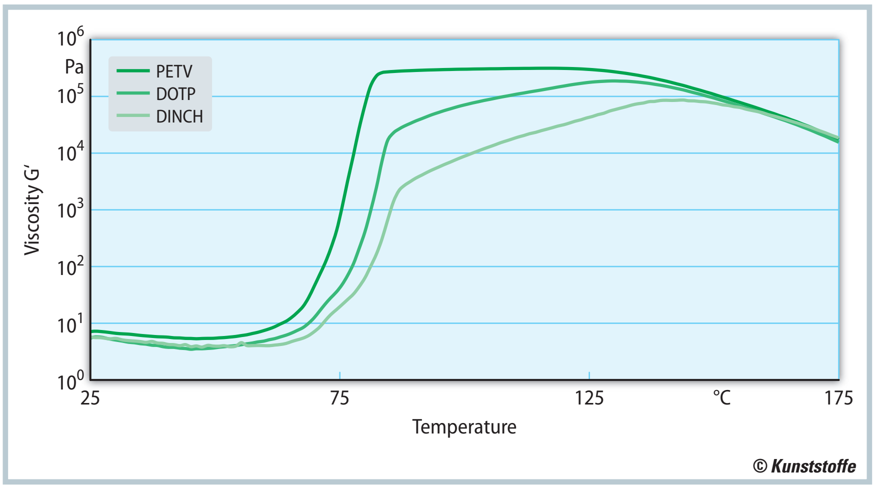


**Fig. 5.** The rheology of the three test candidates shows that plastisol formulation with PETV proceeds more quickly and at lower temperatures (source: Perstorp)

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- Read the German version of the article in our magazine ***Kunststoffe*** or at ***www.kunststoffe.de*** of the time and temperature. Another crucial factor for the formulation as well as the processing and extrusion effectiveness of S-PVC is the absorption speed.

The course of the memory module over the temperatures (**Fig. 5**) shows the transition from the liquid to the viscous and solid state. One can clearly see that this process takes place more quickly with PETV and at lower temperatures. PETV consequently consumes less energy and is better suited for the production of large quantities. **Table 2** shows the results for the degree of fusion or gelling over time. The higher the elongation, the faster processing will be and the higher the productivity. PETV reached 100 % elongation in only 2 minutes at 160 °C. DINCH in comparison reached 70 %.

The absorption diagram shows the time in which phthalate-free plasticizers are absorbed during suspension polymerization (**Fig. 6**). Here, too, PETV is considerably faster than the comparable plasticizers. This result is also significant for processing and productivity.

PVC materials with phthalate-free plasticizers such as those introduced in the test are in demand for applications in direct contact with consumers. These includes, among others, floor coverings, coated textiles, or mats for sports. ■

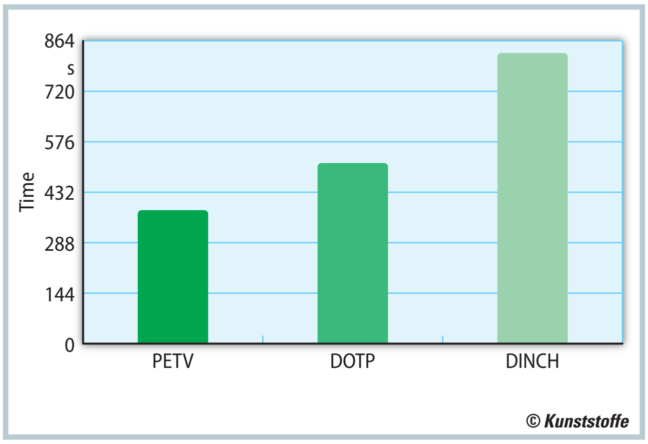


**Fig. 6.** The absorption diagram shows the time in which phthalate-free plasticizers are absorbed in suspension PVC (source: Perstorp)