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ORIGINAL PAPER

Solutions to reduce release behavior of plasticizers out of PVC-made equipments: binary blends of plasticizers and thermal treatment

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Abstract In order to reduce migration of plasticizers out of polyvinyl chloride (PVC), several techniques were attempted. First, binary blends of plasticizers were added to PVC, migration was decreased 100 or 1,000 times as compared to PVC samples containing only one plasticizer: the diffusion coefficient was of the order of 10^{-8} cm^2 s^{-1} for the blend di-2-ethylhexylphthalate (DEHP)/di-2-ethylhexylterephthalate (TDHP) or 10^{-9} cm^2 s^{-1} for the blend DEHP/DBP. A thermal treatment of PVC samples containing only one plasticizer leads to diffusion coefficients of the order of 10^{-10} cm^2 s^{-1}. This second method was also applied to PVC samples plasticized with binary blends. It lowers even more migration of both plasticizers out of PVC. But no particular phenomena were observed with ternary blends of plasticizers introduced in PVC.

Keywords Plasticizer · PVC · Diffusion · Thermal treatment · Binary blends · DEHP

Introduction

The polyvinyl chloride (PVC) makes it possible to realize reliable medical equipments, it is used to manufacture urine bags, catheters, blister packs for pills,

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etc. To carry an open heart surgery through to a successful conclusion, PVC is essential as only PVC-made drains can stand up torsion without appearance of flexures. And the storage of blood would not be possible without bags made of PVC, only this material is authorized because it is the only reliable one for this application [1–4].

The softness of PVC are partially due to the presence of plasticizers (phthalates, adipates, citrates, etc.) in the material. If this material remains the most suitable one for medical equipments, the release behavior of plasticizers from PVC can rightfully bother Public Health Services. In fact, plasticizers contained in PVC of blood bags partially migrate into blood or into human organism during an intravenous administration for example.

Drawbacks are already limited by using phthalates rather than citrates which tend to migrate more easily from PVC packages [5].

To reduce the percentage of plasticizer in PVC could remove the softness of material: the glass transition temperature, T_g, increases by decreasing the amount of plasticizer [6–9]. To assure elastic properties at ambient temperature, not less than 35% of di-2-ethylhexylphthalate (DEHP) was added to PVC. Then T_g is below 0 °C for this percentage whichever analyse method (DMA or DSC) is chosen [10, 11].

Some treatment methods are found to reduce plasticizer migration from PVC materials. For example, UV-irradiation to PVC sheets decreased the amount of DEHP migration by 50% without changing the percentage of plasticizer in PVC [12]. However, techniques applied to reduce release behavior of plasticizer must be more performed.

So we attempted to study release behavior of phthalates [di-2-ethylhexyl adipate (DOA), DEHP, di-2-ethylhexylterephthalate (TDHP), etc.] from plasticized PVC before and after thermal treatment. Several various plasticized PVC sheets were also processed by mixing PVC with binary blends of phthalates. Their influence on the plasticizers migration from sheets was also studied.

Experimental

Material and chemicals

Polyvinyl chloride is a commercial resin (Fluka) in white powder form ($M_n = 25{,}900$ g mol^{-1}, $M_w = 54{,}800$ g mol^{-1}). Plasticizers were used as received: DEHP (Aldrich), TDHP (Aldrich), dibutylphthalate (DBP: Aldrich), Sebacate (di-2-ethylhexyl ester: Aldrich), DOA (Acros).

The other chemicals used to process plasticized PVC samples are *n*-heptane (Acros) and methanol (SDS).

Preparation of the plasticized PVC samples

In order to control the composition of the studied material, it is processed in our laboratory as following. One or several plasticizers are mixed to methanol. Then, PVC is added to this solution in order to obtain a homogeneous mixture.

Afterwards, this mixture was oven-dried at 60 °C to completely evaporate. The remaining compounds (plasticizer(s) + PVC) were pressed into sheets (0.1 cm thick) in a steel mold at 140 °C and under a 100-bar pressure.

Analyses were carried out on different pieces of a sheet, they attest that plasticizer was homogeneously dispersed.

The total amount of plasticizer(s) in PVC samples was always 35% on a mass rate.

Test for determining the rate of plasticizer transfer

In order to test the rate of plasticizer transfer, the various PVC samples were soaked in a liquid, *n*-heptane, according to the following conditions. Diffusion experiments (labeled migration tests) were conducted in a closed flask (50 cm^3) while kept at 30 ± 0.5 °C at a controlled stirring rate. One PVC disk (18 mm diameter) was immersed in 20 cm^3 of *n*-heptane. At various times, the plasticizer which has migrated into the liquid was analyzed by gas chromatography (Thermoquest Trace CG) after the addition of DOA as an internal standard. The stationary phase was 5% diphenyl-95% poly(dimethylsiloxane), Rtx-5 (Thermoquest). The results can be described by the basic equation for unsteady-state diffusion, so called Fick's second law, thus diffusion coefficient D can be determined as described in previous results [11].

Thermal treatment

Some plasticized PVC samples were submitted to thermal treatment in order to study its influence on limiting plasticizer transfer. The first stage consists in soaking PVC disks in *n*-heptane for a short time (4 min) at 30 °C. In the second stage, the disks were dried at 200 °C for 40 s. Afterwards, the rate of plasticizer transfer was tested as described in previous paragraph.

Results and discussion

We have proceeded to migration test as described before in "Experimental".

Interesting properties were displayed by studying plasticized PVC with 35% of DBP as the diffusion coefficient D_0 was very low, that is to say $6 \times 10^{-9}\ \mathrm{cm}^2\ \mathrm{s}^{-1}$. But other plasticized PVC with 35% of DEHP or TDHP must not be left even if their D_0 is respectively 10 or 100 times as important as the D_0 of the PVC containing DBP (Table 1). Indeed, Gonzalez et al. [13] have proved great compatibility between PVC and all these plasticizers.

In order to more reduce migration of phthalate from PVC, binary blends of plasticizers were mixed with PVC. Van Oosterhout and Gibert [14] have determined better performance for binary or ternary blends as compared to only one plasticizer in PVC. D_0 will indicate the diffusion coefficient of a plasticizer when it is the only one in PVC so called "monoplasticized PVC", D'_0 the diffusion coefficient of a plasticizer when it is mixed with another one in PVC pointed out "biplasticized

Table 1 Diffusion coefficient of aromatic plasticizers in PVC for untreated PVC (monoplasticized and biplasticized)

Plasticizer (% : on a mass ratio in PVC)	**D_0 (cm^2.s^{-1})**	Binary blend of plasticizers (% : on a mass ratio in PVC)	**D'_0 (cm^2.s^{-1})**
TDHP (35)	$2,5\ 10^{-7}$	*TDHP (17,5) + DEHP (17,5)*	$9,4\ 10^{-8}$ $7,3\ 10^{-8}$
DEHP (35)	$6,8\ 10^{-8}$	*DEHP (17,5) + DBP (17,5)*	$10,2\ 10^{-9}$ $9,2\ 10^{-9}$
DBP (35)	$6,0\ 10^{-9}$		

PVC". The index "2" for diffusion coefficients will design value obtained after thermal treatment, for example D_2 will be the diffusion coefficient of the only plasticizer added in PVC. By carrying out a migration test, synergistic effects were obtained on biplasticized PVC, treated PVC, and "triplasticized PVC".

Binary blends of plasticizers

For biplasticized PVC containing DEHP and TDHP, the D'_0 is equal to 7.3×10^{-8} cm^2 s^{-1} for DEHP and 9.4×10^{-8} cm^2 s^{-1} for TDHP, that is to say a value similar of the D_0 of DEHP (6.8×10^{-8} cm^2 s^{-1}) when it is the only plasticizer in PVC (Table 1). For plasticized PVC containing only TDHP, the D_0 was ten times as much. So DEHP imposes migration rate of the binary blend DEHP/TDHP. And the use of TDHP becomes moreover conceivable as TDHP migrates more slowly out of PVC, by adding binary blend DEHP/TDHP.

A similar reasoning can be applied for PVC plasticized with the binary blend DEHP/DBP where DBP imposes the migration rate out of PVC (Table 1).

When a binary blend is used to plasticize PVC, the compound which has the lowest D_0 in monoplasticized PVC samples imposes the migration rate from biplasticized PVC. It could mean that interactions between the two plasticizers are created to the detriment of interactions with PVC, and they are so strong that the plasticizers do not fastly diffuse out of PVC. The fastest plasticizer is retained by the slowest one. It can be explained by chemical formulae which are very similar: DEHP has ester groups substitution in position "para" like DBP, but alkyl chains which follow ester function are branched (Fig. 1). DEHP and TDHP have exactly the same chemical formula, but substitution group is in position “ortho” for DEHP, and in position “para” for TDHP.

So, these similarities explain strong interactions between these compounds. However, synergistic effects are not observed any more with binary blends sebacate/DEHP and DOA/DEHP (Table 2). Indeed, for binary blends, the D'_0 of both the plasticizers were an intermediate value between the diffusion coefficient D_0 of every one. In fact, sebacate or DOA belong to aliphatic phthalates class, whereas DEHP is an aromatic phthalate. So interactions between DOA (or sebacate) and DEHP can be

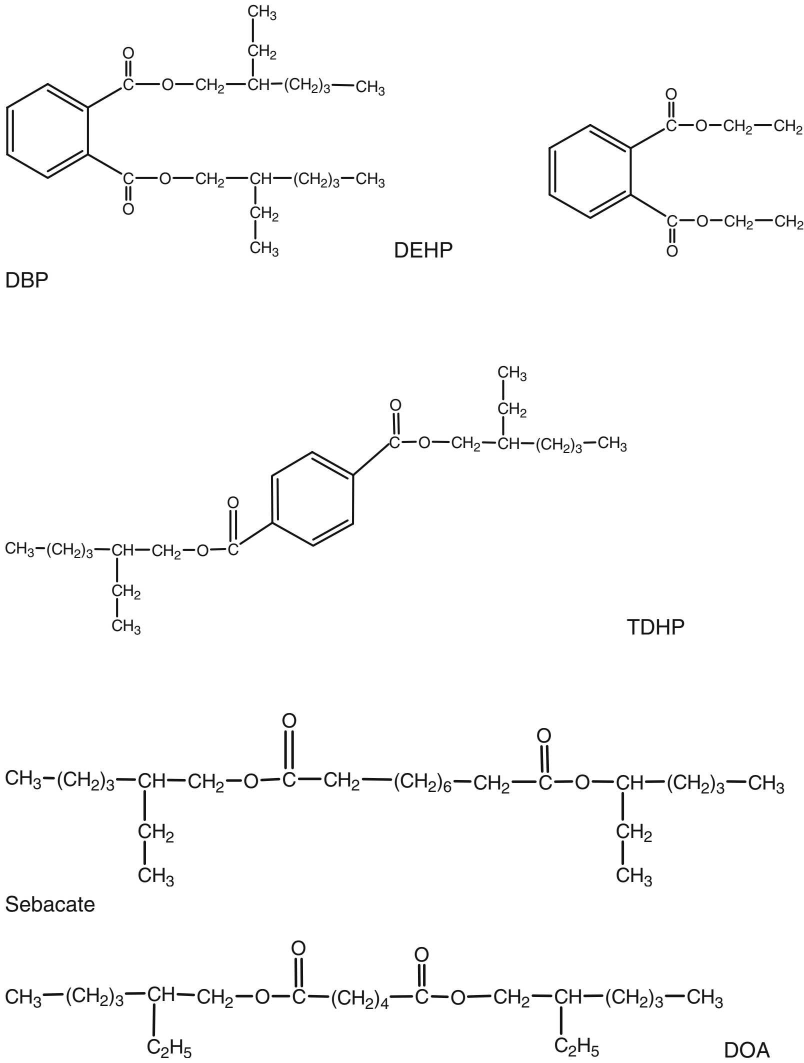

Fig. 1 Chemical formulae of plasticizers

Table 2 Diffusion coefficient of aliphatic plasticizers or DEHP in untreated PVC (monoplasticized and biplasticized)

Plasticizer (% : on a mass ratio in PVC)	$\mathbf{D_0}$ ($\mathbf{cm^2.s^{-1}}$)	Binary blend of plasticizers (% : on a mass ratio in PVC)	$\mathbf{D'_0}$ ($\mathbf{cm^2.s^{-1}}$)
DOA (35)	$7,2.10^{-7}$	*DOA (17,5)* + *DEHP (17,5)*	$2,1.10^{-7}$ $1,5.10^{-7}$
DEHP (35)	$6,8\ 10^{-8}$	*DEHP (17,5)* + *Sebacate (17,5)*	$1,5\ 10^{-7}$ $2,4\ 10^{-7}$
Sebacate (35)	$7,1\ 10^{-7}$		

supposed less strong than these established between two aromatic phthalates DEHP/DBP or DEHP/TDHP.

Thermal treatment

Using binary blends to plasticize PVC tends to decrease the D'_0 of every plasticizer when compared to D_0 for PVC containing only one of them. However, the thermal treatment that “mono”plasticized PVC undergoes remains more efficient than binary blends as D_2 are about 10^{-10} cm^2 s^{-1}, whichever plasticizer is studied (Table 3). The values of D_2 or D'_2 are about 10–1,000 lower than the values D'_0 obtained with binary blends (Tables 1, 2). This treatment also triggers off other consequences, it gets delay time appeared to observe plasticizer starting to leave out of PVC (Fig. 2). This time depends on the nature of plasticizer. DEHP and TDHP have similar chemical formula but delay times (t_R and t'_R) are different: 60.2 h for DEHP and 221.9 h for TDHP (Table 3).

Previous results enable us to understand that structure changes could be brought about by thermal treatment: treated PVC sample is like a sandwich material, it consists in the original plasticized PVC between two sheets of PVC without a plasticizer (Fig. 3). This morphology has been also proved by rheological studies that we have carried previously [10, 11].

To leave out of treated PVC, DEHP must create interactions more easily with unplasticized PVC of borderline sheets, hence a shorter delay time t_R in comparison with TDHP. So the fastness of DEHP diffusion (in comparison with TDHP) must be attributed to better affinity with PVC.

Table 3 Diffusion coefficients and delay times of plasticizers in treated PVC (monoplasticized or biplasticized)

Plasticizer (% : on a mass ratio in PVC)	**Delay time t_R (h)**	**D_2 ($cm^2.s^{-1}$)**	Binary blend of plasticizers (% : on a mass ratio in PVC)	**Delay time t'_R (h)**	**D'_2 ($cm^2.s^{-1}$)**
TDHP (35)	221,9	$2,3\ 10^{-10}$	*TDHP (17,5)*	82.4	$3,4\ 10^{-10}$
			+		
DEHP (35)	60,2	$8,5\ 10^{-10}$	*DEHP (17,5)*	85.3	$2,6\ 10^{-10}$
			DEHP (17,5)	0	$1,7\ 10^{-10}$
			+		
DBP (35)	0	$1,6\ 10^{-10}$	*DBP (17,5)*	0	$7,1\ 10^{-10}$
DOA (35)	3,8	$3,2\ 10^{-10}$			

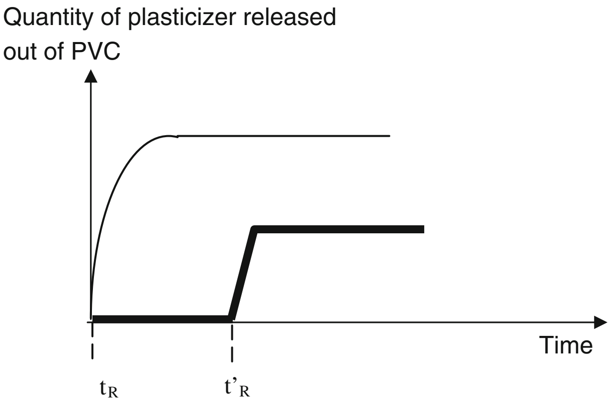

Fig. 2 General profile of the quantity of plasticizer released out of PVC as a function of time. To observe plasticizer to start, a delay time is necessary: t_R for untreated PVC and t'_R for treated PVC

Despite a similar chemical formula for DEHP and TDHP, the boiling temperature of TDHP (400 °C) is more important than this one of DEHP (384 °C). It implies much more intermolecular interactions between TDHP molecules. It would mean that this phenomenon would reduce interactions between PVC and TDHP, with

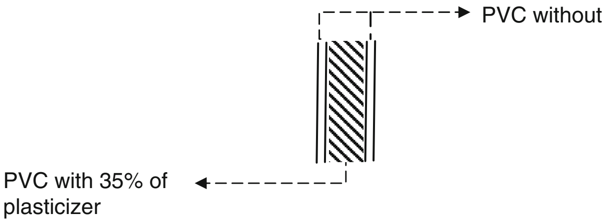

Fig. 3 Schema of a plasticized PVC disk (thickness profile), side after thermal treatment

Table 4 solubility parameters of PVC and various plasticizers

Compound	PVC	DBP	DOA	Sebacate	DEHP	TDHP
δ (cal$^{1/2}$ cm$^{-3/2}$)	9.4	9.3	8.7	8.6	7.9	8.0
$\Delta\delta$ (cal$^{1/2}$ cm$^{-3/2}$) = δ(PVC) − δ(plasticizer)	–	0.1	0.7	0.8	1.5	1.4

These values were found in Polymer Handbook, 4th edition [15]

respect to DEHP. Intermolecular interactions between TDHP molecules are possible because the second ester group is in “para” position from the first one (Fig. 1). On the contrary, one of the substitution ester groups is in “ortho” position from the other one in DEHP, it results in intramolecular interactions or in steric hindrance, restricting intermolecular interactions. This contributes to increase affinity between PVC and DEHP, as a comparison with TDHP. So a shorter delay time to observe DEHP release out of PVC.

A more amazing result was observed with DBP, the delay time t_R was brought down to zero. It means that greater compatibility could not be expected between PVC and any plasticizer but DBP. Indeed, it can be explained by the solubility parameters δ for DBP and PVC which appear very close: the variation $\Delta\delta$ tends to 0.09 cal$^{1/2}$ cm$^{-3/2}$ (Table 4) [14]. On the contrary, DEHP and TDHP migrate from PVC with delay times superior to zero (60.2 and 221.9 h), and their solubility parameters are different from the δ value of PVC, the variation $\Delta\delta$ is equal to 1.40 cal$^{1/2}$ cm$^{-3/2}$ for DEHP and 1.39 cal$^{1/2}$ cm$^{-3/2}$ for TDHP. A relative comparison can be established for delay times, starting from the smallest: DBP < DOA < DEHP < TDHP. If another relative comparison deals with $\Delta\delta$, a similar order is found: DBP < DOA < DEHP < TDHP. Finally, a smaller delay time means more interactions between PVC and the plasticizer. Similar results about compatibility between PVC and some plasticizers were obtained by other researchers [13, 16].

Exceptionally, PVC monoplasticized with sebacate was treated by soaking it in heptane for 1 min instead of 4 min (Table 5). Nevertheless, the value t_R equal to zero seems to mean a good compatibility between sebacate and PVC. In fact, sebacate acts as a more efficient plasticizer than DEHP or TDHP, when they are studied in identical experimental conditions. A comparison can be established for delay times t_R, starting from the smallest: sebacate < DEHP < TDHP. A similar

Table 5 Diffusion coefficients and delay times of plasticizers in treated PVC (monoplasticized or biplasticized)

Plasticizer (% : on a mass ratio in PVC)	**Delay time t_R (h)**	**D_2 ($cm^2.s^{-1}$)**	Binary blend of plasticizers (% : on a mass ratio in PVC)	**Delay time t'_R (h)**	**D'_2 ($cm^2.s^{-1}$)**
TDHP (35)	96,7	9,9 10^{-10}	*TDHP (17,5)* +	14,3	2,0 10^{-10}
DEHP (35)	14,6	8,5 10^{-10}	*DEHP (17,5)*	14,4	1,4 10^{-10}
			DEHP (17,5) +	7,7	4,1 10^{-10}
Sebacate (35)	0	8,9 10^{-9}	*Sebacate (17,5)*	7,5	1,1 10^{-9}

order is determined with their $\Delta\delta$ (=δ(PVC) − δ(plasticizer)) (Table 4). It confirms better affinity of sebacate (with PVC) by comparison with DEHP and TDHP.

Thermal treatment applied to binary blends

For PVC monoplasticized with DEHP or TDHP, the thermal treatment gets appeared delay times t_R of 60.2 and 221.9 h, respectively. In PVC biplasticized with DEHP and TDHP, t'_R are equal to 85.3 h for DEHP, and 82.4 h for TDHP (Table 3). These similar values of t'_R are an intermediate result of every t_R (60.2 h for DEHP and 221.9 h for TDHP), nevertheless the difference between the values t'_R and t_R of DEHP is smaller than the difference $|t'_R - t_R|$ for TDHP. So, the plasticizer, DEHP, which has appeared slower than TDHP before thermal treatment, still imposes the migration mechanism after treatment on biplasticized PVC.

The binary blend DEHP/DBP is even more noteworthy as t_R is equal to zero for both the plasticizers, DEHP and DBP. Besides, it is exactly the value of t_R for DBP when it is the only plasticizer in PVC. Finally, the slower plasticizer of the blends seems to show better affinity with PVC, so it imposes the delay time t'_R (Table 3).

But, such a behavior was not observed for the binary blend DEHP/sebacate (Table 2) even if a delay time t_R equal to zero was noticed for treated PVC monoplasticized with sebacate. The values t'_R, 7.7 h for DEHP and 7.5 h for sebacate, are an intermediate result between t_R of DEHP (14.6 h) and t_R of sebacate

(0 h). This fact can be also explained by the aromatic nature of DEHP whereas sebacate is an aliphatic phthalate, resulting in less important interactions between them.

Finally, no plasticizer imposes the migration mechanism in PVC, when the blend consists in an aliphatic phthalate and an aromatic one.

Ternary blends of plasticizers

No synergistic effects appear, the values of D'_0 seem to be an intermediate result of D_0. The same reasoning as sebacate, an aliphatic phthalate, is blended to aromatic phthalates DEHP and TDHP (Table 6).

Conclusion

Different techniques were tested in order to reduce migration of plasticizers out of PVC. First, binary blends of plasticizers were mixed with PVC to study their performance as compared with PVC containing only one plasticizer. Aromatic blends of phthalates (TDHP/DEHP and DEHP/DBP) reveal synergistic effects: when an aromatic plasticizer was observed to fastly migrate out of PVC, another study was carried out by blending it with another aromatic phthalate. In PVC mixed with a binary and aromatic blend, the plasticizer which initially migrated too fastly has a diffusion coefficient close to the value of the slowest phthalate with which it is blended. For the binary blend DEHP/TDHP, both these aromatic phthalates has a coefficient of the order of 10^{-8} cm^2 s^{-1}, it has been also the value determined when the slowest phthalate, DEHP, is the only plasticizer in PVC. With the binary blend DEHP/DBP, it is DBP that has imposed the release rate with a coefficient of the

Table 6 Diffusion coefficient of plasticizers in PVC for untreated PVC (monoplasticized and plasticized with a ternary blend of phthalates)

Plasticizer (% : on a mass ratio in PVC)	**D_0 ($cm^2.s^{-1}$)**	Ternary blend of plasticizers (% : on a mass ratio in PVC)	**D'_0 ($cm^2.s^{-1}$)**
DEHP (35)	6,8 10^{-8}	*DEHP (11,7)* + *TDHP (11,7)* + Sebacate *(11,7)*	1,8 10^{-7}
TDHP (35)	2,5 10^{-7}		2,9 10^{-7}
Sebacate (35)	7,1 10^{-7}		4,3 10^{-7}

order of 10^{-9} cm^2 s^{-1} because it is the slowest of both them. This synergy was explained by important interactions created between both the plasticizers which belong to an identical class of phthalates, the aromatic phthalates. On the contrary, no synergistic effects were obtained with the binary blends DEHP/DOA and DEHP/sebacate where DEHP is an aromatic phthalate and the other ones are aliphatic. The values obtained for these binary blends (of the order of 10^{-7} cm^2 s^{-1}) result in an average of the diffusion coefficients determined in PVC that contains only DEHP and this with only the aliphatic phthalate.

The second technique consists in a thermal treatment of the PVC samples that contains only one plasticizer. Whichever plasticizer we added to PVC, the diffusion coefficients were all of the order of 10^{-10} cm^2 s^{-1} only after this treatment. So, this thermal treatment contributes to effectively soften the release behavior of the plasticizers. This fact can be explained by structural changes consequent on the thermal treatment: then, the PVC sample looks like a sandwich material (the original material between two thin sheets of PVC without plasticizer). More precisely, differences can be noticed with either plasticizer. And a greater affinity (quantified by the solubility parameter δ) induces a slower migration of the plasticizer out of PVC, and a lower delay time. A relative comparison has been established starting from the more compatible one with PVC and the more retained in PVC: DBP > DOA > DEHP > TDHP. In PVC that contains binary blends of aromatic plasticizers, synergistic effects do not disappear after the thermal treatment. And the plasticizer which has appeared the slowest one in a binary blend still imposes the migration rate after this treatment.

No synergy was noticed when a ternary blend of plasticizers was used, as two aromatic phthalates were blended to an aliphatic one.

A study will be carry out to verify if synergistic effects can be obtained with binary or ternary blends of aliphatic plasticizers and if they reveal greater performance than the aromatic phthalates.

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