Designing Green Plasticizers: Influence of Molecule Geometry and Alkyl Chain Length on the Plasticizing Effectiveness of Diester Plasticizers in PVC Blends.

Hanno C. Erythropel[a], Sarah Shipley[a], Aurélie Börmann[b], Jim A. Nicell[c], Milan Maric[a], Richard L. Leask[a]*

A: McGill University, Department of Chemical Engineering, 3610 University Str, Montréal, QC, H3A0C5, Canada

B: Technische Universität München, Chemistry Department, Lichtenberger Str. 4, D-85747 Garching bei München, Germany

C: McGill University, Department of Civil Engineering and Applied Mechanics, 817 Sherbrooke St W, Montréal, QC, H3A0C3, Canada

*corresponding author:

richard.leask@mcgill.ca

tel +1(514) 398-4270

fax +1(514) 398-6678

Abstract

The influence of central structure and side chain length on plasticizer effectiveness of succinate and maleate diesters blended into poly(vinyl chloride) (PVC) was assessed by tensile testing, DMTA, and surface hardness measurements. While no significant differences between central structures with similar side chain lengths were found, the length of the side chain played an important role, and maximum effectiveness was found for the linear dihexyl esters. In comparison to commercial plasticizers such as DEHP and Hexamoll® DINCH®, succinates and maleates with linear side chains of four to eight carbons performed as well or better in several of the mechanical tests. Earlier work had established that the proposed succinate and maleate compounds exhibited higher biodegradation rates than DEHP, and pending toxicity studies, they seem to be viable replacement compounds for DEHP.

Keywords: PVC Plasticizer Effectiveness; Succinate; Maleate

Highlights:

- Development of green plasticizers to replace phthalates
- Evaluation of mechanical properties of linear succinate and maleate diesters
- Highest plasticizer effectiveness for dihexyl succinate and maleate
- No added benefit of ethyl branch in di (2-ethylhexyl) compounds
- Several compounds of both series performed as good or better than DEHP and DINCH®

Introduction

Plasticizers are typically relatively small molecules that are incorporated into polymeric materials in order to increase the workability, flexibility, or distensibility of the matrix polymer [1]. Plasticizers are added to hard and brittle polymers such as poly(vinyl chloride) (PVC), resulting in lower melt viscosity, lower glass transition temperature (T_g), lower elastic modulus, and better elongation of the blend, or any combination of these properties [2].

Due to the vast variety of polymers and plasticizers that exist, and the very different chemical moieties present in these materials, there are multiple theories on the mechanisms of plasticization that complement each other (i.e., the lubricity-, gel-, and free volume theories). In brief, there exist interactions between the polymer chains in the case of PVC due to the dipole present on each (δ+) C-Cl (δ-) bond. Due to this weak dipole, chains interact with neighboring chains, thereby creating a network that, when below the T_g, does not permit significant chain mobility, resulting in macroscopic brittleness. Once the T_g is reached, there is sufficient energy to overcome the attractive forces between the chains, thereby allowing for more chain movement within the blend, and then the material becomes macroscopically flexible [2-4]. The role of the plasticizer is to break up some of these chain-chain interactions, resulting in lowering the T_g which in turn influences the material properties of the final product. To achieve the separation of neighboring polymer chains, the plasticizer should contain non-polar or slightly polarizable portions, yet a plasticizer that is too non-polar would be immiscible with PVC. For this reason, a plasticizer molecule will usually contain polar moieties (i.e., ester groups) that will interact with the PVC chains to assure compatibility, as well as non-polar groups (i.e., alkyl chains) that break up the chain-chain interactions and play the main role in the plasticizing effect [2-5].

In 2008, 5.6 million metric tonnes of plasticizer were produced to plasticize PVC, with phthalate diesters accounting for 88 % of this production. Of these phthalate diesters, di (2-ethylhexyl) phthalate (DEHP; sometimes misleadingly called DOP) accounted for 54 % of production in 2008 [6], making DEHP the most important industrial plasticizer (see Figure 1 for the structure). Since added plasticizers (also called external plasticizers) are not chemically bound to the polymer matrix, they tend to leach out over time, ultimately ending up in the environment, where they preferentially accumulate in hydrophobic matter [7-11]. DEHP and its breakdown products have been considered ubiquitous environmental contaminants as early as the 1980s, being found in soils, water, the atmosphere, and in house dust [10, 12, 13]. DEHP degradation happens primarily under aerobic conditions and temperature plays an important role [7, 10]. When DEHP is broken down by hydrolysis, it yields two stable metabolites; i.e., its monoester MEHP and 2-ethyl hexanoic acid, which is the oxidation product of the liberated 2-ethyl hexanol [14, 15]. Extensive studies on these compounds have been carried out, which show a wide range of toxic effects [14-23]. The monoester MEHP has been particularly linked to antiandrogenic activities in humans [24-26].

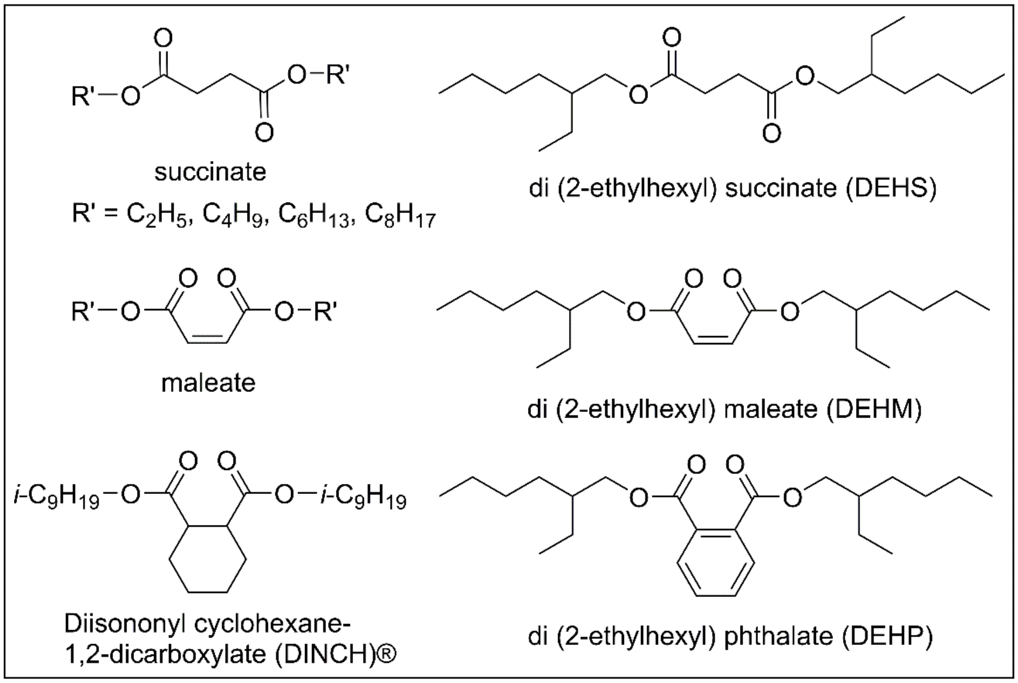

Figure 1: Structures of succinate and maleate diesters and the commercially-available plasticizers DINCH® and DEHP.

Due to their environmental persistence and associated health concerns, several phthalates including DEHP have become increasingly subject to regulation [27-30], resulting in the need to develop safer, and more environmentally compatible alternatives. The choice of a suitable alternative would require an extensive screening process in order to assure comparable plasticizing properties, ideally faster biodegradation rates without the buildup of stable metabolites, reduced toxicity, and reduced leaching. The compound diisononyl cyclohexane-1,2-dicarboxylate (Hexamoll® DINCH®; see Figure 1 for the structure) was introduced by BASF in the early 2000s as a plasticizer for "sensitive applications" [31]. Recently, we proposed series of n-alkyl succinates and -maleates (see Figure 1 for structures) as possible alternatives to DEHP due to the faster biodegradation rates of the parent compound and their metabolites [32-34] and their reduced leaching rates [35]. In our previous studies, the plasticizing ability was assessed only in terms of T_g reduction.

The addition of plasticizer molecules to polymers results in the improvement of mechanical properties, and these improvements are a function of concentration but also of molecular structure [36]. When comparing the effects of different molecular structures on material properties of polymers, both the term "plasticizer efficiency" [36, 37] as well as "plasticizer effectiveness" [38, 39] have been used. Some of the mechanical properties that are improved by the addition of plasticizer are, among others, increased strain at break, reduced tensile strength and modulus, reduced torsional modulus, and reduced surface hardness [2, 36].

In this work, we present more extensive material testing data of our candidate plasticizers to evaluate their plasticizer effectiveness when blended with PVC at equal weight-fractions (to ensure comparability) by tensile testing, dynamic-mechanical thermal analysis (DMTA), and surface hardness measurements. We investigated the effect of central structure, the overall molecule length as determined by the longest chain of oxygen- and carbon-atoms, and the influence of ethyl branches in the β-position to the ester moiety (as present in DEHP) on plasticizer properties. Finally, the results are compared to similar measurements conducted with commercially available DEHP and DINCH®.

2 Methods and Materials

2.1 PVC and Plasticizers

Unplasticized PVC (UPVC; K50) was provided by Solvay Benvic, France. Compounds commercially available were purchased through Sigma-Aldrich, and included di (2-ethylhexyl) phthalate (DEHP, 99 %), diethyl succinate (DES, 99 %), diethyl maleate (DEM, 97 %), and dibutyl maleate (DBM, 96 %). The other commercially used, and marketed as "green", plasticizer diisononyl cyclohexane-1,2-dicarboxylate (Hexamoll® DINCH®, 99 %; called simply DINCH® from here on) was provided by BASF Canada. The other compounds including dibutyl succinate (DBS), dihexyl succinate (DHS), dioctyl succinate (DOS), di (2-ethylhexy) succinate (DEHS), dihexyl maleate (DHM), dioctyl maleate (DOM), and di (2-ethylhexyl) maleate (DEHM) were synthesized in our laboratories using Dean-Stark esterification, as described previously [34]. The structures of these plasticizers are indicated in Figure 1.

2.2 Extrusion of PVC/Plasticizer Blends

The blending of UPVC with the plasticizers was achieved with a conical intermeshing twin-screw extruder (Haake Minilab, Thermo Electron Corporation), with conical screws of 5/14 mm diameter and a length of 109.5 mm. The batch size was 3 g. Mixing of UPVC with the plasticizer was achieved in a two-step process. First, a blend of 20 parts per hundred rubber (phr; equivalent to 16.6 wt.-%) was prepared, then the plasticizer content was raised to 40 phr in a second extrusion step by addition of more plasticizer into the compounded blend. This two-step procedure was necessary to ensure the homogeneity of the resulting blends. The extruder was operated at 130 °C during the first step to 20 phr and at 110 °C in the second step to achieve 40 phr, with a screw speed of 30 rpm, which was raised to 60 rpm after 5 min of each 3g batch to push out the remaining material. In the first step, 4 phr of epoxidized soy bean oil (Chemtura Corporation) as heat stabilizer and 5 phr of stearic acid (Fisher Scientific) as lubricant were added in addition to the appropriate amount of plasticizer. In the second step the remainder of the plasticizer was added (without other additives). Each extruded batch was recycled through the extruder a second time, meaning that each 40 phr blend tested had passed through the extruder for a total of 4 passes.

2.3 Production of Test Bars for Tensile Testing and Dynamic Mechanical Thermal Analysis

Test bars were produced by pressing the finely chopped blends containing 40 phr of plasticizer (28.6 wt.-%) in a hot press (Carver manual Hydraulic Press, with Watlow temperature controllers). Type V test bars were used for tensile testing according to ASTM D-638, with the following dimensions: 1.5 mm thickness, 3.25 mm width of narrow section (W), 15.5 mm length of narrow section (L), 32.5 mm distance between grips (D), 63.5 mm overall length (LO), and 10 mm width overall (WO) [40]. The rectangular test bars for DMTA were produced according to the ASTM D-4065 method, with the following dimensions: 1.5 mm thickness, 10 mm width, and 50 mm length [41]. The rectangular DMTA test bars were also suitable for hardness testing by nanoindentation according to the ASTM E-2546 method [42]. All test bars were conditioned in a desiccator at room temperature for a minimum of 48 h prior to testing.

2.4 Tensile Testing

Tensile testing was carried out on a Yamazu Easy Test with a load cell of 500 N according to ASTM D-638 [40]. The exact dimensions of the middle section were recorded (Electronic Outside Micrometer, Fowler Tools & Instruments), and n = 5 specimens (except for DBM, DOS with n = 4) per blend were tested at a strain rate of 5 mm/min. The stress-strain curves (see examples shown in Figure 2) were used to obtain values for strain and stress at break. To calculate the apparent modulus, the derivative of a polynomial curve fit to the experimental data (R^2 value of at least 0.98) was calculated to determine the apparent modulus at 15 % elongation (EL), 25 %EL, and 50 %EL as shown in Figure 2, but only the values for 25 %EL are reported for all blends in Table 1.

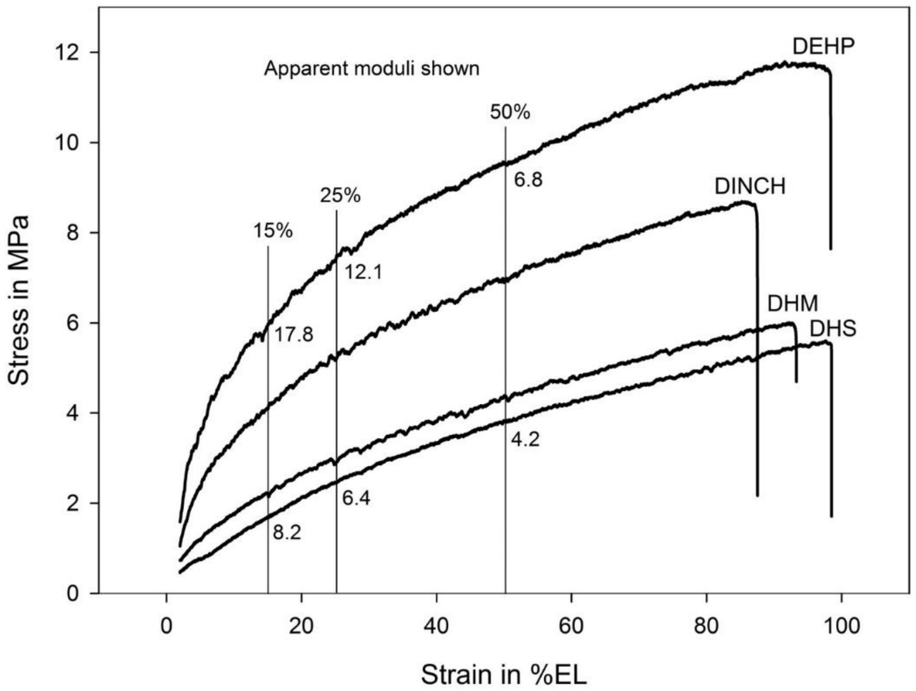

Figure 2: Selected tensile stress-strain curves for 40 phr blends of PVC with DEHP, DINCH®, DHM and DHS. Estimated values of apparent moduli at 15 %, 25 % and 50 % elongation (in MPa) are shown for DEHP (top values), and DHS (bottom values).

2.5 Dynamic Mechanical Thermal Analysis (DMTA)

DMTA was carried out on a rheometer with fixed bottom clamp and a moveable top clamp (Anton Paar MCR302 with SRF12 fixtures and CTD450 convection oven, Anton Paar GmbH). The convection oven was operated with nitrogen gas purge to avoid oxidation of the specimens. The exact dimensions of the middle section were recorded (Electronic Outside Micrometer, Fowler Tools & Instrument). DMTA was run in torsion mode, strain-controlled with an amplitude gamma of 0.01 %. A temperature sweep from 25 °C to 100 °C at a rate of 2 °C/min at a constant shear rate of 1 Hz was carried out for each blend, with the machine controlling the normal force set to -0.5 N. The software RheoPlus (V3.61, Anton Paar GmbH) was used to obtain the storage modulus G’, and the loss modulus G”.

2.6 Hardness Testing

The surface hardness of the various blends was determined using a micro-indenter (Nanovea PB1000 with Nano module, stainless steel ball tip of 1 mm diameter). Measurements were done at room temperature and repeated three times on each test bar, with each test conducted in a different third of the length of the test bar. Once the indenter had reached the zero point, it subsequently built up a contact load of 0.3 mN, and then forced the tip into the sample at a rate of 30 mN/min until a load of 20 mN was reached. The tip was then removed at the same rate of 30 mN/min. During the experiment, indentation depth was recorded automatically by the software (Nanovea Nano Hardness Tester). A Matlab® program was used to calculate the surface hardness according to ASTM E-2546 (2007). In brief, this calculation is based on a stiffness term derived from the slope of the first third of the unloading curve, as well as the estimated contact area and indentation depth, with the result expressed in units of MPa.

2.7 Statistics

Statistical analysis was performed using GraphPad Prism 5 software, for one-way- and two-way ANOVA tests with Bonferroni post-tests. A p value less than 0.05 was interpreted as significant, with $p < 0.05$ represented by *, $p < 0.01$ by **, and $p < 0.001$ by ***.

Table 1: Properties of 40 phr blends of PVC and different plasticizers. Averages and standard deviations are reported for n specimens, as indicated. Structures of plasticizers are shown in Figure 1.

	Tensile strength			**DMTA torsion**		**Surface hardness**
Plasticizer	**Strain at break (%EL)[a]**	**Max stress (MPa)[a]**	**Apparent modulus at 25 %EL (MPa)[a]**	**G’ at 1Hz, 25 °C (MPa)**	**G” at 1Hz, 25 °C (MPa)**	**Nano-indentation (MPa)[b]**
DES	102 ± 6	9.3 ± 0.2	10.0 ± 0.3	34.0	12.0	2.59 ± 0.24
DBS	107 ± 4	5.7 ± 0.2	6.3 ± 0.3	8.7	2.1	0.69 ± 0.13
DHS	99 ± 6	5.5 ± 0.2	6.4 ± 0.3	7.5	2.1	0.54 ± 0.07
DOS	87 ± 4[c]	6.5 ± 0.3[c]	7.4 ± 0.2[c]	31.0	9.2	1.02 ± 0.09[d]
DEM	105 ± 3	9.9 ± 0.2	10.3 ± 0.3	35.9	14.2	1.70 ± 0.31
DBM	109 ± 5[c]	6.3 ± 0.4[c]	7.2 ± 0.1[c]	6.7	1.4	0.74 ± 0.17[d]
DHM	92 ± 6	5.9 ± 0.2	6.8 ± 0.2	6.5	2.0	0.51 ± 0.05
DOM	92 ± 4	6.6 ± 0.2	7.4 ± 0.3	23.8	7.3	0.93 ± 0.04
DEHS	99 ± 6	6.7 ± 0.2	7.9 ± 0.2	17.0	5.9	0.78 ± 0.07
DEHM	96 ± 5	7.0 ± 0.2	8.4 ± 0.2	17.0	6.4	1.08 ± 0.18
DEHP	96 ± 4	11.8 ± 0.1	12.1 ± 0.6	7.6	3.1	0.44 ± 0.05[a]
DINCH®	87 ± 5	8.8 ± 0.4	9.1 ± 0.2	32.9	11.8	1.64 ± 0.53

[a] n = 5; [b] n = 3; [c] n = 4; [d] n = 2

3 Results

3.1 Tensile Strength

All samples exhibited strain softening during tensile testing, obtained stress-strain curves are thus non-linear as shown, for example, in Figure 2 for blends with DEHP, DINCH®, DHM, and DHS. Averages of stress at break, strain at break, and apparent modulus at 25 %EL are reported in Table 1.

3.1.1 Strain at Break

The data for strain at break is reported in Table 1 and visualized in Figure 3a), where results for blends with the commercial plasticizers DEHP and DINCH® are shown first. These are followed by blends with the series of succinate and maleate plasticizers, in ascending order of linear side chain length from C2 (diethyl; "DE") to n-C8 (dioctyl; "DO"). This is followed by the respective branched di (2-ethylhexyl) compound ("DEH"), which is not part of the series of unbranched alkyl side chains, but only compared to the equally-long dihexyl ("DH") compound, and the dioctyl ("DO") compound, which is of equal molecular weight.

There was a significant effect of chain length on strain at break (two-way ANOVA, $p < 0.0001$), yet the central group structure had no effect (two-way ANOVA, $p = 0.64$) for our candidate plasticizers. DBS and DBM had the highest means of strain at break observed within their respective series, which were significantly higher than commercial DEHP (one-way ANOVA, Bonferroni post-test: DBS, $p < 0.05$; DBM, $p < 0.01$) and commercial DINCH® (one-way ANOVA, Bonferroni post-test: DBS, $p < 0.001$; DBM, $p < 0.001$). DOS and DOM had the lowest strain at break within their respective series, but were not significantly different from commercial DEHP (one-way ANOVA, Bonferroni post-test, $p > 0.05$, respectively) or DINCH® (one-way ANOVA, Bonferroni post-test, $p > 0.05$, respectively). Thus, we conclude that all compounds performed as well or better than the commercial plasticizers in terms of increasing strain at break.

While no significant difference between the equally long DHS and DEHS was observed (one-way ANOVA, Bonferroni post-test, $p > 0.05$), DOS was significantly lower than the compound with the same molecular weight, DEHS (one-way ANOVA, Bonferroni post-test, $p < 0.05$). No statistical difference between DHM and the equally-long DEHM was observed (one-way ANOVA, Bonferroni post-test, $p > 0.05$), nor between the compound of equal molecular weight, DOM and DEHM (one-way ANOVA, Bonferroni post-test, $p > 0.05$).

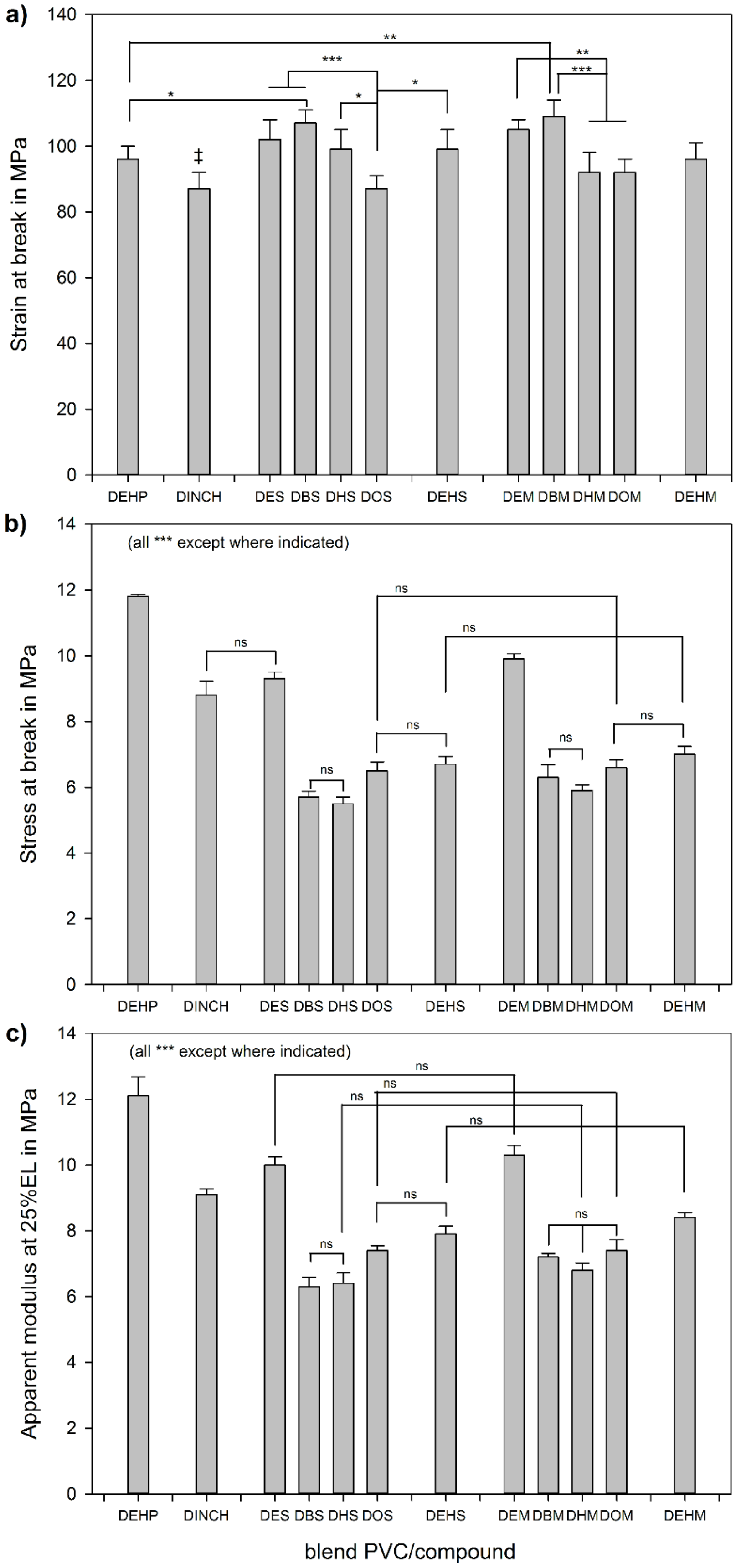
a)
Strain at break in MPa
0
20
40
60
80
100
120
140
*
**
***
*
*
**
***
‡
DEHP
DINCH
DES
DBS
DHS
DOS
DEHS
DEM
DBM
DHM
DOM
DEHM
b)
Stress at break in MPa
(all *** except where indicated)
0
2
4
6
8
10
12
14
ns
ns
ns
ns
ns
ns
ns
DEHP
DINCH
DES
DBS
DHS
DOS
DEHS
DEM
DBM
DHM
DOM
DEHM
c)
Apparent modulus at 25%EL in MPa
(all *** except where indicated)
0
2
4
6
8
10
12
14
ns
ns
ns
ns
ns
ns
ns
DEHP
DINCH
DES
DBS
DHS
DOS
DEHS
DEM
DBM
DHM
DOM
DEHM
blend PVC/compound

Figure 3: Strain at break (a), stress at break (b), and apparent modulus at 25 %EL (c) for blends of PVC/plasticizer at 40 phr. Averages and standard deviations of n = 5 specimens are shown, with the exception of DBM and DOS with n = 4. (a) ‡ DINCH® strain at break results were statistically significantly different from: DES**, DBS***, DHS*, DEHS*, DEM***, DBM***; (b) All stress at break results were statistically significantly different (***) except where shown (and except DES versus DEM **; DBS vs DBM **; DHS vs DHM *); (c) All apparent modulus results were statistically significantly different (***) except where shown (and except DBS versus DBM **).

3.1.2 Stress at Break

The data for stress at break are presented in Table 1 and Figure 3b). There was a significant effect of chain length on the stress at break (two-way ANOVA, $p < 0.0001$), as well as an effect of central group structure (two-way ANOVA, $p < 0.0001$) for our candidate plasticizers.

All tested compounds exhibited significantly lower means for stress at break compared to DEHP (one-way ANOVA, Bonferroni post-test, $p < 0.001$), for which the highest ultimate tensile stress was observed. Regarding the other commercial plasticizer, DINCH®, only DEM (the plasticizer blend with the highest stress at break among the maleates) showed a higher stress at break (one-way ANOVA, Bonferroni post-test, $p < 0.01$). The succinate with the highest stress at break recorded, DES, was shown to not differ significantly from DINCH® (one-way ANOVA, Bonferroni post-test, $p > 0.05$). Similar to DEHP, all other compounds showed significantly lower averages for stress at break compared to DINCH® (one-way ANOVA, Bonferroni post-test, $p < 0.001$).

When comparing the equally long DHS to DEHS and also DHM to DEHM, the unbranched DH-compounds showed significantly lower values than the DEH-compounds (one-way ANOVA, Bonferroni post-test, $p < 0.001$, respectively). However, when comparing the molecules of equal molecular weight, DOS to DEHS, and DOM to DEHM, no significant statistical difference between the means was observed (one-way ANOVA, Bonferroni post-test, $p > 0.05$, respectively).

3.1.3 Apparent Modulus at 25 % Elongation

According to ASTM D-638 [40], the modulus of elasticity is preferably reported, however, no linear portion was present in the recorded curves (as shown in Figure 2). For non-linear behavior, it is suggested in ASTM D638 that the secant modulus be reported, which is obtained by drawing a secant from the origin to a set strain [40]. Given the differences between the obtained curves, especially in the first third of the curves (i.e., compare DEHP to DHS in Figure 2), reporting secant moduli would exaggerate the differences between the recorded curves and thus not accurately describe our observations (Figure 2 contains examples of stress-strain curves for four different compounds). Instead, we used the apparent modulus, which corresponds to the slope of the curve at a defined strain. As shown in Figure 2 for three different strains (15 %EL, 25 %EL, and 50 %EL), and for two curves (DEHP and DHS), the apparent modulus did not result in as large a difference between curves as the secant modulus did, while accounting for the change in slope as the elongation increases. In Table 1 we show the results for the apparent modulus at 25 %EL for all experiments.

The data for the apparent modulus are presented in Table 1 and visualized in Figure 3c). A significant effect of chain length on the apparent modulus at 25 %EL was observed (two-way ANOVA, $p < 0.0001$), as well as an effect of central group structure (two-way ANOVA, $p < 0.0001$) for our candidate plasticizers.

All tested compounds exhibited significantly lower means for apparent modulus at 25 %EL compared to DEHP (one-way ANOVA, Bonferroni post-test, $p < 0.001$). This indicates that blends with DEHP were the stiffest specimens tested. The stiffest compounds within the series of succinates and maleates were DES and DEM, respectively, which were significantly less stiff than DEHP (one-way ANOVA, Bonferroni post-test, $p < 0.001$), but stiffer than DINCH® (one-way ANOVA, Bonferroni post-test, $p < 0.001$). The least stiff compounds within the series of succinates were DBS and DHS, which were not found to differ significantly (one-way ANOVA, Bonferroni post-test, $p > 0.05$). A slight increase in stiffness was observed for the longest compound in the series, DOS, which was significant compared to the aforementioned DBS and DHS (one-way ANOVA, Bonferroni post-test, $p < 0.001$). Within the series of maleates, DBM, DHM, and DOM showed the lowest stiffness and all three means were not significantly different from each other (one-way ANOVA, Bonferroni post-test, $p > 0.05$).

The unbranched DHS was found to exhibit a lower stiffness than the equally long but branched compound DEHS (one-way ANOVA, Bonferroni post-test, $p < 0.001$), yet for the compounds of equal molecular weight, DOS and DEHS, no significant difference between the means was found (one-way ANOVA, Bonferroni post-test, $p > 0.05$). For the maleates, a significant difference between both the equally long DHM and DEHM (one-way ANOVA, Bonferroni post-test, $p < 0.001$), as well as the molecules of equal molecular weight DOM and DEHM was observed (one-way ANOVA, Bonferroni post-test, $p < 0.001$).

3.2 Torsional DMTA

For all blends, DMTA was performed with a temperature sweep from 25 °C to 100 °C at a constant frequency of 1 Hz. Two exemplary curves of storage (G') and loss (G") moduli for blends of PVC/DEHP and PVC/DHS are shown in Figure 4, and the results for the other compounds can be found in Figures S1-S11 in the supplementary data. Table 1 summarizes the results of G' and G" only at 25 °C since the general trends were the same for all tested blends. Values at 25 °C were chosen since this condition is closest to room temperature.

As shown by the torsional data in Table 1, in both series of succinates and maleates, the shortest compound, DES and DEM, had the highest torsional moduli (G' and G"). Moreover, as the chain length increased, torsional modulus decreased with a minimum reached at side chain lengths around four to six carbons (DBS, DHS, and DBM, DHM). The torsional modulus increased again slightly for the compounds with n-C8 side chains, DOS and DOM. All branched DEH compounds (DEHS, DEHM, DEHP) show values at similar levels, comparable to DOM, but higher than the DB and DH compounds, which showed the least torsional stiffness of all compounds. DINCH® and DOS showed values slightly higher than DEHP.

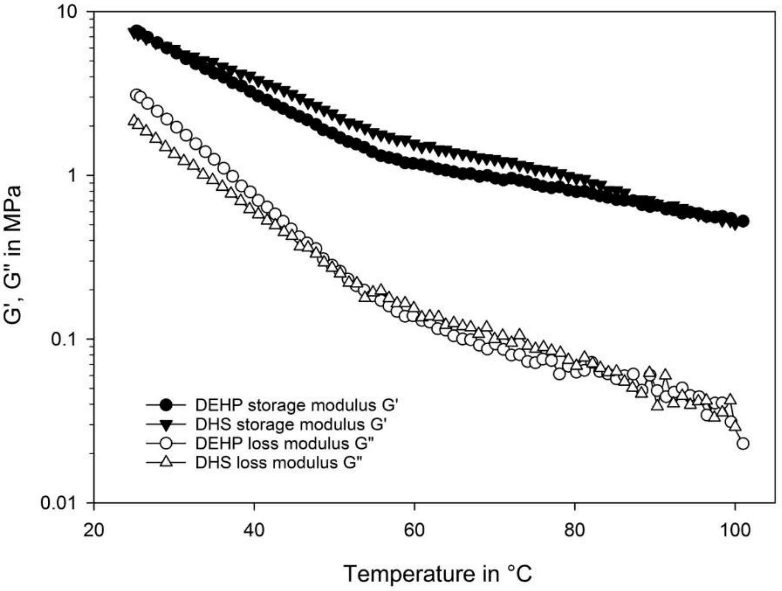

Figure 4: Selected plots of DMTA torsional temperature sweep for 40 phr blends of PVC with DEHP and DHS. Storage modulus G' (filled symbols) and loss modulus G" (open symbols) are shown.

3.3 Surface Hardness by Nano-indentation

The results obtained for the surface hardness of the blends of PVC with the various plasticizers are presented in Table 1 and visualized in Figure 5. A significant effect of chain length on surface hardness was observed (two-way ANOVA, $p = 0.0025$), as well as an effect of central group structure (two-way ANOVA, $p < 0.0001$).

The blends with the highest surface hardness in the succinate and maleate series were those plasticized with the diethyl compounds, DES and DEM, respectively. While DEHP was significantly softer than DES and DEM (one-way ANOVA, Bonferroni post-test, $p < 0.001$), DINCH® was only softer than DES (one-way ANOVA, Bonferroni post-test, $p < 0.001$), while no significant difference in hardness was observed between DEM and DINCH® (one-way ANOVA, Bonferroni post-test, $p > 0.05$). All other members of the succinate and maleate series did produce hardness values slightly above that for DEHP, yet no significant difference was observed (one-way ANOVA, Bonferroni post-test, $p > 0.05$). This means that all plasticizer candidates rendered the surface of PVC softer than commercially-available DINCH®, and similarly soft as DEHP, with the exception of the diethyl compounds.

No significant differences in surface hardness were observed between the equally-long DHS and DEHS, and also DHM and DEHM, respectively (one-way ANOVA, Bonferroni post-test, $p > 0.05$), nor between the molecules of equal molecular weight, DOS and DEHS, and also DOM and DEHM (one-way ANOVA, Bonferroni post-test, $p > 0.05$).

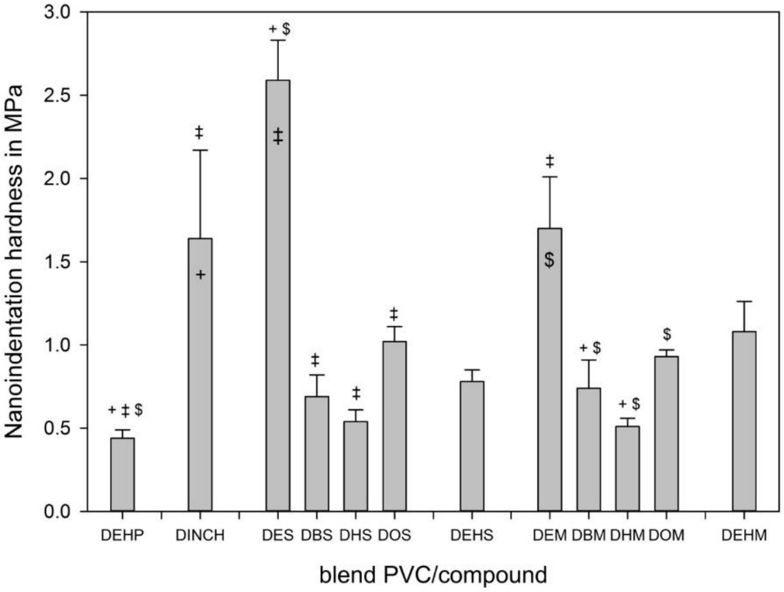

Figure 5: Surface hardness (in MPa) for blends of PVC/compound at 40 phr. Averages and standard deviations are shown for n = 3 measurements, with the exception of DBM and DOS (n = 2) and DEHP (n = 5). Symbols above error bars indicate statistically significant differences ($p < 0.05$, Bonferroni post-test) with respect to DINCH® (+), DES (‡), and DEM ($).

4 Discussion

As DEHP and phthalates are increasingly considered to be compounds of concern, alternative plasticizers that are less problematic for human health and environmental stability must be developed.

However, if these compounds are to be viable replacements for DEHP and other commercially-available phthalates, they should be as effective, or more effective in plasticizing PVC. Here, we tested a series of maleate and succinate diesters with linear side chains, varying from two to eight carbons, including one branched compound with the same branching as present in commercial DEHP. Note that the side chain is incorporated into the diester by the appropriate choice of alcohol in the esterification reaction. Previously, we have shown that the succinates and maleates are readily biodegraded and that metabolites produced were only transient [32, 33]. In the present study, these greener compounds and, for comparison, the commercial plasticizers DEHP and DINCH® were extruded with PVC at 40 phr and these blends were then subjected to a series of tests in order to compare their effectiveness as plasticizer in blends with PVC. We present the results of some standard tests to evaluate the blends regarding their formability (elongation at break), their strength (tensile strength), their stiffness (tensile and torsional moduli), and their durability (surface hardness).

The performance of the plasticizer candidates improved with increasing size, from the smallest compounds (C2 side chains) to the dihexyl compounds (C6 side chains), and then decreased slightly for the longest molecules (C8 side chains). No apparent effect was visible from the addition of ethyl branches in di (2-ethylhexyl) maleate (DEHM) and succinate (DEHS), when compared to the equally-long, but unbranched dihexyl compounds. Particularly, the dihexyl compounds of the maleate and the succinate showed comparable plasticizing effectiveness to DEHP in terms of strain at break and hardness, and better performance in terms of stress at break, and torsional and tensile moduli. The mentioned dihexyl compounds were also more effective in all tested properties when compared to DINCH®.

4.1 Influence of Side Chains

In diester plasticizers, the side chains are often made up of alkyl chains, with their length and the degree of branching imparted through the alcohol used in the esterification reaction. Their primary role is to separate the PVC polymer chains and reduce chain-chain interactions. These result from the weak but permanent dipole present on each carbon-chlorine bond (C(δ+) - Cl(δ-)). The large amount of attractive chain-chain interactions along the backbone of PVC are the cause for the hard and brittle nature of PVC when not plasticized. Alkyl chains are non-polar and almost non-polarizable and therefore, can disrupt the interactions between PVC chains. We wanted to determine whether the length of these side chains had an effect on plasticizing efficiency beyond the data previously reported [5, 43].

We observed an improvement in plasticizing effectiveness as the (unbranched) side chain length was increased (Table 1). From side chain lengths of two to six carbons, the stress at break, apparent modulus, torsional modulus, and hardness improved with increasing side chain length. When the side chain length is increased, which occurs on both sides of the diester, more non-polar groups are added to both sides of the molecule, which in turn can disrupt more PVC chain-chain interactions. This explains the increased plasticizer effectiveness of the succinates and maleates with longer side chains. Curiously, this effect seems to level off once six carbons in the side chain are reached. In fact, for some experiments, there was a deterioration in plasticizing performance of the n-dioctyl compounds (i.e., stress at break, torsional modulus, and surface hardness, see Table 1), meaning that the most effective compounds were those with a side chain length of around six carbons. This deterioration is partly due to the amount of plasticizer within the blends, which is determined by the weight, and not by moles, which is standard procedure in the polymer industry. With increasing side chain length, the molecular weight (MW) of the overall compound increases and therefore, given that the same mass of plasticizer is used in every blend (i.e., 40 phr), the corresponding absolute amount of plasticizer-molecules in the blend decreases (i.e., on molar basis, there would be 14 % more DOS molecules compared to DEHP, or 70 % more DBM molecules compared to DEHP). It has been previously shown that addition of dialkyl phthalates on a molar basis to PVC, rather than a mass basis, did indeed result in a linear increase in T_g reduction efficiency with increasing side chain length, and not the above-described maximum efficiency near the six-carbon compounds [44, 45].

The differing number of moles between samples is not the only explanation why the data in Figures 3b), 3c), and 5 exhibit the afore-mentioned effectiveness maximum near dihexyl compounds. The compatibility of the plasticizers with the PVC resin also plays a role [45]. Several studies have been conducted to investigate the effect of alkyl chain length of diesters on their compatibility with PVC, and similar maxima for compatibility around side chain lengths of six carbons were observed. Compatibility measurements were based on Flory-Huggins theory [46, 47]. Doty and Zable reported such compatibility maxima for dialkyl phthalates and sebacates using osmotic pressure measurements [48]. Anagnostopoulos et al. found compatibility maxima for phthalates (*ortho*-substituted), isophthalates (*meta*-substituted), terephthalates (*para*-substituted), maleates, and fumarates when measuring solid-to-gel temperatures of PVC particles in plasticizers [49, 50]. In a methodologically similar study, Luther et al. also reported such compatibility maxima for phthalates, adipates, and citrates [51]. Note that sebacates and adipates differ from succinates only in the length of the central chain that connects the two ester functions. Similarly, Würstlin and Klein reported similar curves for phthalates and a matrix of saturated diesters varying both in central chain length (C2-C10) and alkyl side chain (C1-C8), through the measurement of the cloud point (i.e., determined by cooling a dilute solution of PVC dissolved in the plasticizer). In fact, the authors found succinates with side chains from four to six carbons to be most compatible with PVC [43, 52].

In all of the above-mentioned studies, the recorded curves went through a local maximum of compatibility between a side chain length of four to six carbons. Stuart et al. focused on the T_g reduction efficiency of dialkyl succinates blended with PVC, as measured by differential scanning calorimetry (DSC), and also found the best performing compound to be dihexyl succinate [53]. The above observations match very well with our own observations as shown in Figures 3b) and 3c), and Table 1.

There also exist other studies that focused on plasticizer effectiveness by material properties measurements rather than compatibility based on fundamental properties as described in the above paragraph. These further support our findings that diesters with unbranched alkyl chains between four and six carbons were the most effective plasticizers. For example, Walter measured the modulus of elasticity of soft PVC gels plasticized with dialkyl phthalates and observed that blends with dibutyl phthalate had the lowest modulus (i.e., and, hence, the best performance) [54], which is similar to the results reported here in Figure 3c) and Table 1.

4.2 Influence of Branching

For each maleate and succinate, one branched diester was tested, in which the side chains resembled those of DEHP, meaning that the alcohol used to esterify the diacid was 2-ethylhexanol. We compared the results of these compounds specifically to the corresponding dihexyl compound as these are similar in overall molecular length (i.e., the longest chain of carbon- and oxygen atoms), with the only difference being the ethyl-branch on the β-carbon in the side chain of the di(2-ethylhexyl) (DEH) compounds. Additionally, we compared the DEH-succinate and -maleate to the corresponding di-n-octyl compounds as these are of similar molecular weight.

Results indicate that there were no added benefits in terms of plasticizer effectiveness for either the succinates or the maleates when the ethyl-branch was present, which has previously been described for phthalates [55]. In fact, for stress at break and apparent modulus, the ethyl branches seemed to have a negative effect on these properties when compared to the equally long DH compounds. It seems that the more important factor for plasticizer properties is the overall molecule length.

With the exception of strain at break, no difference between the compounds of equal molecular weight, DEHS/DOS, and DEHM/DOM were observed. Similar observations were reported previously by Würstlin and Klein for dialkyl phthalates, where in every case the branched phthalates showed a poorer T_g reduction efficiency compared to their unbranched counterparts of equal molecular weight [44].

4.3 Influence of Central Structure

The central structure of diesters played an equally important role as the side chains with respect to plasticizer effectiveness. Purely non-polar compounds containing only alkyl chains would not be compatible with PVC due to the inherent polar nature of the PVC chains. This means that in order to retain the non-polar part of the plasticizer - which plays the more active role in plasticization (i.e., the alkyl chain part) - within the PVC matrix, one or more polar parts that interact with PVC are also needed. However, the polarity of these groups must be of the same order of magnitude as the PVC polarity, otherwise there would not be a sufficient interaction between the two and phase separation would occur. Diesters have been shown to have the required degree of polarity, thus rendering diester molecules good candidates for PVC plasticizers [5, 56].

As indicated in Figure 1, the maleate contains a double bond between the two central carbon atoms, thereby locking the orientation of the two ester groups towards one another in the shown *cis* position. Both dipoles inherent to the ester groups would be pointing essentially in the same general direction (i.e., δ- on the carbonyl oxygen, and δ+ on the carbonyl carbon), allowing this compound to interact with one or two PVC chains at two different locations. The same would apply to DEHP, where the ester groups are also in a similar position to one another. The specific orientation of the diester molecules towards one another has also been shown to play an important role in its plasticizer effectiveness: that is, in previous work, we were able to show that the fumarate molecule, a structural isomer to the maleate except for the positioning of the ester bonds towards one another, did not reduce the T_g in blends with PVC as effectively as the maleate [34]. In the fumarate, the ester groups are in a *trans* position relative to one another, resulting in the dipoles of the ester groups pointing in different directions. Finally, in the saturated succinate molecule, there is no double bond present, with the result that the succinate is free to rotate around the central bond. Because of this, the succinates would be free to take the most advantageous position for interaction with PVC chains within the polymer matrix. In earlier work, we showed that T_g reduction efficiency of succinates and maleates were at comparable levels [32, 33], and similar observations were made in this study for several other material properties.

The structure of DINCH® is slightly more complicated, due to presence of the cyclohexane ring, which unlike the phthalate is not planar and can take on a range of spatial conformations. The “chair”-conformation is generally the most stable conformation, especially when bulky substituents are present (see Figure 6) [57]. In a 1,2-disubstituted cyclohexane such as DINCH®, these substitute groups are on neighboring carbons of the ring and can be in *cis*- and in *trans* positions relative to each other, as shown in Figure 6 (a), b): *trans*, c), d): *cis*) [57]. Additionally, due to the cyclic structure of cyclohexane, substituents can be in an equatorial position and in an axial position, resulting in the four possibilities shown in Figure 6; the first row (a) and b) shows the *trans*-configuration, in which both substituents can either be in the equatorial (Figure 6a)) or the axial position (Figure 6b)). In a *trans*-DINCH®, the favorable conformation would be the one in which both bulky substituents are positioned equatorially (Figure 6a)), due to the reduced steric interaction with neighboring atoms, as compared to the axial position (Figure 6b)) [57]. For a *cis*-DINCH®, one substituent has to be in axial and one in equatorial position, which means that there is no preferred conformation between those shown in Figures 6c) and 6d) when both substituents are similar, as is the case for DINCH®.

No detailed information was provided by the supplier on the composition of the DINCH® sample we tested (which also contains structural isomers stemming from the mixture of alcohols used to create the ester bond), so it is assumed that the sample likely consisted of a mixture of *cis*/*trans* isomers. In such a mixture, one would thus expect the conformations a), c), and d) in Figure 6 to be predominantly present. Upon examination, it can be seen that all three conformations are more closely related to the maleate in terms of the ester positioning than the fumarate (i.e., compare Figure 1 to Figures 6a), c), d)). Only the axial conformation of the *trans*-DINCH® (Figure 6c)) would resemble the fumarate rather than the maleate but, as explained above, this configuration is sterically unfavorable. Taken together, this explains why DINCH® is an effective plasticizer.

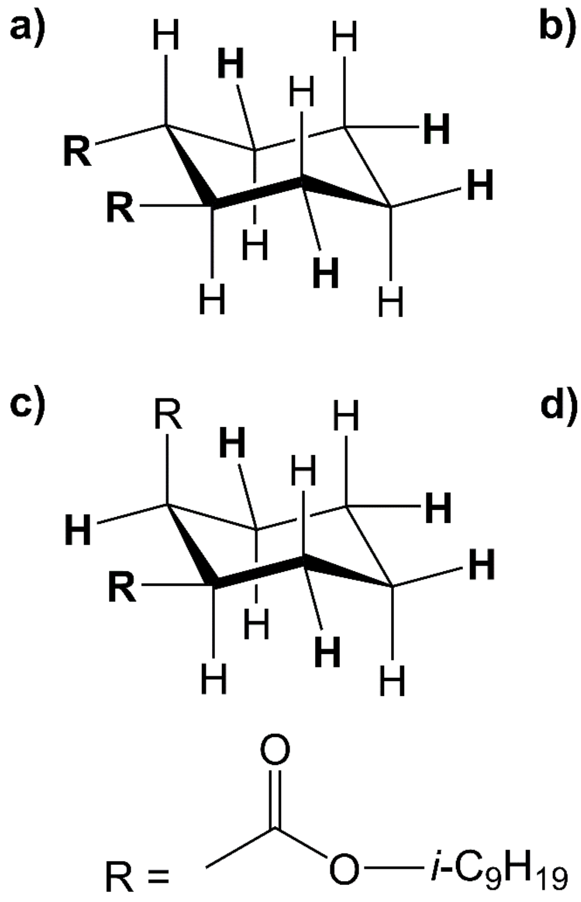

Figure 6. Cyclohexane in the “chair” conformation with equatorial substituents indicated in bold: (a) R-substituents *trans* and in equatorial position; (b) R-substituents *trans* and in axial position; (c) and (d) R-substituents *cis* with one substituent in axial and one substituent in equatorial position.

However, for some of the experiments carried out in this study, the plasticizer performance of DINCH® was lower compared to DEHP and the maleates with chain lengths of four carbons (i.e., when comparing stress at break, apparent modulus, torsional modulus, and surface hardness). This suggests that the positioning of the ester groups relative to one another is not as advantageous in DINCH® as in DEHP or the maleates with side chains of at least four carbons. Given that DINCH® is likely a mixture of isomers, this is not surprising and similar experiments conducted with pure *cis*- and *trans*-DINCH®

would bring more insight. Comparing plasticizer effectiveness of DINCH® to the succinates with side chains of at least four carbons, similar results were found: that is, values for stress at break, apparent modulus, torsional modulus, and surface hardness were lower for the succinates, indicating higher plasticizer effectiveness. In both DINCH® and the succinate, the carbonyl groups are linked by two saturated carbons, but rotation around the central bond is only possible in the succinate. In DINCH® rotation cannot occur due to the presence of the cyclohexyl-ring (see Figure 1). In earlier work, we demonstrated that the ability of the central chain to rotate plays an important role in T_g reduction effectiveness [33], and the results for the mechanical properties tested in this study further support this.

Overall, whenever a side chain length of at least four carbons was present in our candidate plasticizers, members of both series of compounds showed comparable or higher plasticizer effectiveness than the commercial plasticizers. In comparison to DEHP, better performance was found for stress at break and apparent modulus. However, in comparison with DINCH®, the mentioned succinates and maleates with side chains of at least four carbons showed better performance with respect to stress at break, apparent modulus, torsional modulus, and surface hardness. Differences between the succinate and maleate series seemed rather minor, from which we conclude that from a plasticizing effectiveness standpoint, both central structures make such molecules feasible alternatives to DEHP and DINCH®.

4.4 Global Structural Considerations

A credible alternative plasticizer must be one that is not only an effective plasticizer in comparison with current commercially-available compounds, but it must also be less hazardous to the environment and human health. In this work, we focused primarily on evaluating the plasticizing effectiveness of compounds in terms of final PVC formulation material properties for which green characteristics had already been observed [32, 33].

From Table 1, the dibutyl- and dihexyl compounds DBS, DBM, DHS, and DHM stand out as the compounds with the highest plasticizer effectiveness within their respective series, but also when compared to the commercial plasticizers DEHP (with lower stress at break, apparent modulus, and torsional modulus, and comparable strain at break and surface hardness) and DINCH® (with higher strain at break and lower stress at break, apparent modulus, torsional modulus, surface hardness). Additionally, these compounds also lowered the T_g more efficiently than DEHP [32, 33].

Higher plasticizer efficiency is important as it means that a smaller mass of plasticizer would need to be incorporated into PVC to obtain the desired product properties. Such an effect could possibly overcome the higher cost premium that these compounds may have relative to DEHP or other current commercial plasticizers.

As alluded to above, the mechanical properties alone are not the only important characteristics that need to be considered when designing alternative plasticizers, but important factors including biodegradation, environmental persistence and toxicity must also be given due consideration. Earlier work focused on assessing the biodegradability of the succinate and maleate plasticizer candidates compared to DEHP [32, 33] and additional studies with respect to toxicity are ongoing. An added important advantage that one alternative plasticizers may have over another would be if the compound could be produced from renewable resources. In this respect, succinate diesters could be of particular interest because of the increased fermentative production capacities of succinic acid [58], which could lead to a product that is more fully in line with the principles of green chemistry [59].

5 Conclusion

Our results lend further support to earlier findings that: (1) within the diesters of a central-chain length of four carbons, an unsaturated compound in *cis* position is about as effective as the saturated compound [34]; (2) between such compounds, the length of the side chain plays a more important role than the central structure [32, 33]; and (3) free rotation around the central bond plays an important role in the plasticizer effectiveness of saturated compounds [33].

We have demonstrated that diester plasticizers based on succinic and maleic acid with linear side chains between four and eight carbons in length are as effective as commercially-available DEHP and DINCH® in terms of plasticizing PVC resin, and for some tests even improved mechanical properties were apparent. The length of the alcohol used to create the ester bonds, which determines the alkyl side chain length of the diester, had a strong influence on plasticizer properties: for both succinates and maleates, the compounds with a side chain length of four to six carbons showed the highest plasticizer effectiveness. In terms of alkyl branching within the molecule, adding an ethyl-branch (such as that present in DEHP) did not improve plasticizer performance, but instead deteriorated some mechanical properties. When comparing the two central groups (i.e., saturated, and non-saturated in *cis* configuration), some differences were observed, but these were minor. Taken together, this suggests that the right choice of alcohol to produce diesters with a certain side chain length is as important as the choice of the central structure to produce effective plasticizers.

Acknowledgements

The authors acknowledge BASF Canada for their donation of a sample of Hexamoll® DINCH®. This research was supported by grants from the Canadian Institute of Health Research (CIHR; grant RHF-100626 of the Institute of Human Development, Child and Youth Health), and the Natural Sciences and Engineering Research Council of Canada (NSERC; Discovery Grants Program, 261938-13). Student support was provided through a McGill Engineering Doctoral Award (MEDA) of the Faculty of Engineering of McGill University and a Bourse d’Excellence pour Étudiants Étrangers (PBEEE V1) of the Fonds de Recherche du Québec – Nature et Technologies (FRQNT).

References

1. ASTM D-883 - Standard Terminology Relating to Plastics, 2012.
2. J.K. Sears, J.R. Darby, The Technology of Plasticizers, John Wiley, New York, 1982.
3. G. Wypych, Handbook of Plasticizers, second Ed., ChemTec Publishing, Toronto, 2012.
4. F. Würstlin, Weichmachung, in: K.A. Wolf, R. Nitsche, (Eds.), Kunststoffe. Struktur, physikalisches Verhalten und Prüfung. Erster Band: Struktur und physikalisches Verhalten der Kunststoffe, Vol. 6, Springer-Verlag, Berlin, Heidelberg, 1962, pp. 769-790.
5. O. Leuchs, Zur Weichmachung von Polyvinylchlorid, Kunststoffe 46 (1956) 547-554.
6. M.D. Bisig, Plasticizer market update, 20th Annual Vinyl Compounding Conference, Ponte Vedra Beach, FL, 2009.
7. H.C. Erythropel, M. Maric, J.A. Nicell, R.L. Leask, V. Yargeau, Leaching of the plasticizer di (2-ethylhexyl) phthalate (DEHP) from plastic containers and the question of human exposure, Appl. Microbiol. Biotechnol. 98 (2014) 9967-9981.
8. G. Heinemeyer, C. Sommerfeld, A. Springer, A. Heiland, O. Lindtner, M. Greiner, T. Heuer, C. Krems, A. Conrad, Estimation of dietary intake of bis (2-ethylhexyl) phthalate (DEHP) by consumption of food in the German population, Int. J. Hyg. Environ. Health 216 (2013) 472-480.
9. U.S. Agency for Toxic Substances and Disease Registry: Toxicological profile for Di (2-ethylhexyl) phthalate (DEHP), Atlanta, GA, 2002.
10. T.J. Wams, Diethylhexylphthalate as an environmental contaminant - a review, Sci. Total Environ. 66 (1987) 1-16.
11. C.A. Staples, D.R. Peterson, T.F. Parkerton, W.J. Adams, The environmental fate of phthalate esters: A literature review, Chemosphere 35 (1997) 667-749.
12. K. Becker, M. Seiwert, J. Angerer, W. Heger, H.M. Koch, R. Nagorka, E. Rosskamp, C. Schluter, B. Seifert, D. Ullrich, DEHP metabolites in urine of children and DEHP in house dust, Int. J. Hyg. Environ. Health 207 (2004) 409-417.
13. W. Butte, W. Hoffmann, O. Hostrup, A. Schmidt, G. Walker, Endocrine disrupting chemicals in house dust: results of a representative monitoring, Gefahrst. - Reinhalt. Luft 61 (2001) 19-23.
14. O. Horn, S. Nalli, D. Cooper, J. Nicell, Plasticizer metabolites in the environment, Water Res. 38 (2004) 3693-3698.
15. S. Nalli, D.G. Cooper, J.A. Nicell, Biodegradation of plasticizers by *Rhodococcus rhodochrous*, Biodegradation 13 (2002) 343-352.
16. B.T. Akingbemi, R.T. Youker, C.M. Sottas, R.S. Ge, E. Katz, G.R. Klinefelter, B.R. Zirkin, M.P. Hardy, Modulation of rat Leydig cell steroidogenic function by di (2-ethylhexyl)phthalate, Biol. Reprod. 65 (2001) 1252-1259.
17. P.M.D. Foster, E. Mylchreest, K.W. Gaido, M. Sar, Effects of phthalate esters on the developing reproductive tract of male rats, Hum. Reprod. Update 7 (2001) 231-235.
18. M. Gazouli, Z.X. Yao, N. Boujrad, J.C. Corton, M. Culty, V. Papadopoulos, Effect of peroxisome proliferators on Leydig cell peripheral-type benzodiazepine receptor gene expression, hormone-stimulated cholesterol transport, and steroidogenesis: Role of the peroxisome proliferator-activator receptor alpha, Endocrinology 143 (2002) 2571-2583.
19. S.C. Lloyd, P.M. Foster, Effect of mono (2-ethylhexyl) phthalate on follicle-stimulating hormone responsiveness of cultured rat Sertoli cells, Toxicol. Appl. Pharmacol. 95 (1988) 484-489.
20. C.D. Piche, D. Sauvageau, M. Vanlian, H.C. Erythropel, B. Robaire, R.L. Leask, Effects of di (2-ethylhexyl) phthalate and four of its metabolites on steroidogenesis in MA-10 cells, Ecotoxicol. Environ. Saf. 79 (2012) 108-115.
21. J. Fan, K. Traore, W. Li, H. Amri, H. Huang, C. Wu, H. Chen, B. Zirkin, V. Papadopoulos, Molecular mechanisms mediating the effect of mono-(2-ethylhexyl) phthalate on hormone-

stimulated steroidogenesis in MA-10 mouse tumor leydig cells, Endocrinology 151 (2010) 3348-3362.

22. J.H. Richburg, K. Boekelheide, Mono (2-ethylhexyl) phthalate rapidly alters both Sertoli cell vimentin filaments and germ cell apoptosis in young rat testes, Toxicol. Appl. Pharmacol. 137 (1996) 42-50.
23. D.B. Martinez-Arguelles, T. Guichard, M. Culty, B.R. Zirkin, V. Papadopoulos, In utero exposure to the antiandrogen di (2-ethylhexyl) phthalate decreases adrenal aldosterone production in the adult rat, Biol. Reprod. 85 (2011) 51-61.
24. N. Pant, M. Shukla, D.K. Patel, Y. Shukla, N. Mathur, Y.K. Gupta, D.K. Saxena, Correlation of phthalate exposures with semen quality, Toxicol. Appl. Pharmacol. 231 (2008) 112-116.
25. S.H. Swan, K.M. Main, F. Liu, S.L. Stewart, R.L. Kruse, A.M. Calafat, C.S. Mao, J.B. Redmon, C.L. Ternand, S. Sullivan, J.L. Teague, and S.F.F.R. Team, Decrease in anogenital distance among male infants with prenatal phthalate exposure, Environ. Health Persp. 113 (2005) 1056-1061.
26. D.B. Martinez-Arguelles, E. Campioli, M. Culty, B.R. Zirkin, V. Papadopoulos, Fetal origin of endocrine dysfunction in the adult: The phthalate model, J. Steroid Biochem. Mol. Biol. 137 (2013) 5-17.
27. Canadian Hazardous Products Act: Phthalates Regulations, Ottawa, 2010.
28. EU/2005/84/EC, European Union Directive on Phthalates in Toys and Childcare Articles, Brussels, Belgium, 2005.
29. U.S. Consumer Product Safety Improvement Act of 2008, Section 108, Washington D.C., 2008.
30. Bureau Veritas, Revision of Phthalate Requirements in Toys Under Japan Food Sanitation Law, 2010.
31. B.L. Wadey, An innovative plasticizer for sensitive applications, J. Vinyl Addit. 9 (2003) 172-176.
32. H.C. Erythropel, T. Brown, M. Maric, J.A. Nicell, D.G. Cooper, R.L. Leask, Designing greener plasticizers: Effects of alkyl chain length and branching on the biodegradation of maleate based plasticizers, Chemosphere 134 (2015) 106-112.
33. H.C. Erythropel, P. Dodd, R.L. Leask, M. Maric, D.G. Cooper, Designing green plasticizers: Influence of alkyl chain length on biodegradation and plasticization properties of succinate based plasticizers, Chemosphere 91 (2013) 358-365.
34. H.C. Erythropel, M. Maric, D.G. Cooper, Designing green plasticizers: influence of molecular geometry on biodegradation and plasticization properties, Chemosphere 86 (2012) 759-766.
35. J. Kastner, D.G. Cooper, M. Maric, P. Dodd, V. Yargeau, Aqueous leaching of di (2-ethylhexyl) phthalate and "green" plasticizers from poly(vinyl chloride), Sci. Total Environ. 432 (2012) 357-364.
36. C.E. Wilkes, J.W. Summers, C.A. Daniels, PVC Handbook, Hanser Gardner, Cincinatti, OH, 2005.
37. R.F. Boyer, Effect of plasticizers on some physical properties of polymers, TAPPI 34 (1951) 357-362.
38. G.P. Koo, Dynamic mechanical testing of polymers, Plast. Eng. 30 (1974) 33-38.
39. C.M. Sinko, G.L. Amidon, Plasticizer-induced changes in the mechanical rate of response of film coatings: An approach to quantitating plasticizer effectiveness, Int. J. Pharm. 55 (1989) 247-256.
40. ASTM D-638 - Standard Test Method for Tensile Properties of Plastics, 2014.
41. ASTM D-4065 - Standard Practice for Plastics: Dynamic Mechanical Properties: Determination and Report of Procedures, 2012.
42. ASTM E-2546 - Standard Practice for Instrumented Indentation Testing, 2007.
43. F. Würstlin, H. Klein, Ester monofunktioneller Alkohole als PVC-Weichmacher, Kunststoffe 46 (1956) 3-8.
44. F. Würstlin, H. Klein, O-Phthalsäuredialkylester als PVC-Weichmacher, Makromol. Chem. 16 (1955) 1-9.

45. E.H. Immergut, H.F. Mark, Principles of plasticization, in: A.J. Platzer (Ed.), Plasticization and Plasticizer Processes, ACS, 1965. pp. 1-26.
46. P.J. Flory, Thermodynamics of high polymer solutions, J. Chem. Phys. 9 (1941) 660.
47. M.L. Huggins, Some properties of solutions of long-chain compounds, J. Phys. Chem. 46 (1942) 151-158.
48. P. Doty, H.S. Zable, Determination of polymer liquid interaction by swelling measurements, J. Polym. Sci. 1 (1946) 90-101.
49. C.E. Anagnostopoulos, A.Y. Coran, H.R. Gamrath, Polymer-diluent interactions. I. A new micromethod for determining polyvinyl chloride-diluent interactions, J. Appl. Polym. Sci. 4 (1960) 181-192.
50. C.E. Anagnostopoulos, A.Y. Coran, Polymer-diluent interactions. II. Polyvinyl chloride-diluent interactions, J. Polym. Sci. 57 (1962) 1-11.
51. H. Luther, F. Glander, E. Schleese, Mikroskopische Untersuchungen zum Quell- und Lösungsverhalten von Polyvinylchlorid in Weichmachern, Kunststoffe 52 (1962) 7-14.
52. F. Würstlin, H. Klein, Weichmacher-Wirksamkeit in Zusammenhang mit der chemischen Konstitution der Weichmacher, Kolloid Z. Z. Polym. 128 (1952) 136-142.
53. A. Stuart, M.M. McCallum, D.M. Fan, D.J. LeCaptain, C.Y. Lee, D.K. Mohanty, Poly(vinyl chloride) plasticized with succinate esters: synthesis and characterization, Polym. Bull. 65 (2010) 589-598.
54. A.T. Walter, Elastic properties of polvinyl chloride gels, J. Polym. Sci. 13 (1954) 207-228.
55. M. Rahman and C.S. Brazel, The plasticizer market: An assessment of traditional plasticizers and research trends to meet new challenges, Prog. Polym. Sci. 29 (2004) 1223-1248.
56. C.P. Smyth, Dielectric Behavior and Structure: Dielectric Constant and Loss, Dipole Moment and Molecular Structure, McGraw-Hill, New York, 1955.
57. R.J. Ouellette and J.D. Rawn, Organic Chemistry: Structure, Mechanism, and Synthesis, Elsevier, San Diego, 2014.
58. V.G. Debabov, Prospects for biosuccinic acid production, Appl. Biochem. Microbiol. 51 (2015) 787-791.
59. P.T. Anastas and J.C. Warner, Green Chemistry: Theory and Practice, Oxford University Press, New York, 2000.

Figure Captions

Figure 1: Structures of succinate and maleate diesters and the commercially-available plasticizers DINCH® and DEHP.

Figure 2: Selected tensile stress-strain curves for 40 phr blends of PVC with DEHP, DINCH®, DHM and DHS. Estimated values of apparent moduli at 15 %, 25 % and 50 % elongation (in MPa) are shown for DEHP (top values), and DHS (bottom values).

Figure 3: Strain at break (a), stress at break (b), and apparent modulus at 25 %EL (c) for blends of PVC/plasticizer at 40phr. Averages and standard deviations of n = 5 specimens are shown, with the exception of DBM and DOS with n = 4. (a) ‡ DINCH® strain at break results were statistically significantly different from: DES**, DBS***, DHS*, DEHS*, DEM***, DBM***; (b) All stress at break results were statistically significantly different (***) except where shown (and except DES versus DEM **; DBS vs DBM **; DHS vs DHM *); (c) All apparent modulus results were statistically significantly different (***) except where shown (and except DBS versus DBM **).

Figure 4: Selected plots of DMTA torsional temperature sweep for 40 phr blends of PVC with DEHP and DHS. Storage modulus G' (filled symbols) and loss modulus G" (open symbols) are shown.

Figure 5: Surface hardness (in MPa) for blends of PVC/compound at 40 phr. Averages and standard deviations are shown for n = 3 measurements, with the exception of DBM and DOS (n = 2) and DEHP (n = 5). Symbols above error bars indicate statistically significant differences ($p < 0.05$, Bonferroni post-test) with respect to DINCH® (+), DES (‡), and DEM ($).

Figure 6. Cyclohexane in the “chair” conformation with equatorial substituents indicated in bold: (a) R-substituents *trans* and in equatorial position; (b) R-substituents *trans* and in axial position; (c) and (d) R-substituents *cis* with one substituent in axial and one substituent in equatorial position.

Table Headings

Table 1: Properties of 40 phr blends of PVC and different plasticizers. Averages and standard deviations are reported for n specimens, as indicated. Structures of plasticizers are shown in Figure 1.