

# Migration Resistant Polymeric Plasticizer for Poly(vinyl chloride)

Annika Lindström, Minna Hakkarainen

Department of Fiber and Polymer Technology, Royal Institute of Technology, S-100 44 Stockholm, Sweden

Received 25 January 2006; accepted 17 May 2006

DOI 10.1002/app.24777

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Flexible films of poly(vinyl chloride) (PVC) and linear or branched poly(butylene adipate) (PBA), synthesized from 1,4-butanediol and adipic acid or dimethyl ester of adipic acid, were aged in an aqueous environment for 10 weeks to study how branching, molar mass, and end-group functionality affect the leaching of polyester plasticizer from thin films. Principal component analysis was applied to reveal patterns and correlations between mechanical properties, material characteristics, and aging behavior. Introduction of branches in the polyester structure increased the miscibility between PVC and the polyester, resulting in improved

mechanical properties and lower water absorption. Methyl ester end-group in PBA polyester stabilized the polymeric plasticizer toward hydrolysis, and reduced the formation and migration of monomeric degradation products from the blends during aging in water. The combination of branched structure with methyl ester end-groups resulted in a migration resistant polymeric plasticizer. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2458–2467, 2007

**Key words:** poly(vinyl chloride); polyester; blends; degradation; chromatography

## INTRODUCTION

Phthalate plasticizers have been used extensively to impart flexibility in poly(vinyl chloride) (PVC) articles since the 1920s.<sup>1</sup> Phthalate esters are low molar mass compounds that are easily released from the polymer matrix and they are found in most environments, in domestic foods and wastes, and in animals and humans.<sup>2,3</sup> When used in applications like medical devices or toys, the contact with biological fluids accelerates the leaching of low molar mass additives. The loss of plasticizer causes changes in the long-term properties of the material as well as possible toxic and biological effects when the plasticizer is transferred to humans.<sup>3–6</sup> In July 2005, the European Parliament approved the recommendation of a ban forbidding the use of three of the most common phthalate esters, bis(2-ethyl hexyl)phthalate (DEHP), dibutyl phthalate (DBP), and benzyl butyl phthalate (BBP), in toys and childcare articles, within the European Union.<sup>7</sup> The ban also includes the use of three other phthalate esters, diisononyl phthalate (DINP), diisodecyl phthalate (DIDP), and di-*n*-octyl phthalate (DnOP), in toys and childcare articles that can be placed in the mouth. This is an augmentation of previous restrictions<sup>3,8</sup> concerning the use of phthalate plasticizers in toys and childcare articles, and an indication of the

importance of continued research to replace the phthalate plasticizers.

The migration of possibly harmful substances from medical plastics can be prevented by substituting the harmful plasticizer, by substituting the polymer with one that does not need plasticizers, or by preventing the mass transfer from the polymer matrix by surface modification. Among the alternative plastics evaluated, ethylene–vinyl acetate copolymers (EVA), polyesters, polyolefins, and laminates have been found to offer additional property benefits to some applications,<sup>1,4,9</sup> though often at the expense of original application performance. Reducing the mass transfer from the material by surface modification such as surface coating,<sup>10,11</sup> surface crosslinking,<sup>12,13</sup> or by using multi-layered tubing<sup>14,15</sup> also often reduces migration at the cost of other properties such as flexibility, thermal stability, surface characteristics, and appearance.<sup>1</sup> There is thus a large demand for finding alternative plasticizers, and a promising and appealing way to obtain safe plasticized PVC grades is to substitute phthalate esters with compatible and nontoxic polymeric plasticizers.

The use of polymeric plasticizers usually makes the material more difficult to process, increases the tensile strength, and reduces elongation.<sup>16</sup> However, branched polymers have a higher density of chain-ends compared to linear polymers of the same molar mass, and therefore also more free volume and mobility at the same molar mass.<sup>17</sup> Using a branched polymeric plasticizer would thus increase the mobility of the system compared to a system plasticized with a linear

Correspondence to: M. Hakkarainen (minna@polymer.kth.se).

polymer, at the same time the branched polymer's high molar mass and bulkiness significantly reduces its volatility and diffusivity compared to low molar mass plasticizers. PVC has been blended with many different polymers,<sup>16,18–20</sup> among them are aliphatic polyesters. The miscibility of polyester/PVC blends has been shown to be favored by a polyester CH<sub>2</sub>/C=O ratio of 4–10.<sup>21,22</sup> This is one of the reasons why polycaprolactone (PCL)<sup>21,23</sup> and poly(butylene adipate) (PBA)<sup>16,21,22,24</sup> are two of the most frequently used polymeric plasticizers for PVC.

Only a few studies have addressed the migration of polymeric plasticizers from flexible PVC products.<sup>16,24–27</sup> Castle et al.<sup>24</sup> studied the migration of a series of PBA oligomers (from trimer to an oligomer with 11-monomer units) into olive oil. A substantial amount of the plasticizer migrated into olive oil during 12 h and low molar mass oligomers dominated among the migrating species. Monomers and oligomers also migrated from commercial PVC tubes plasticized with linear PBA when aged in water at different temperatures.<sup>25</sup> When aged in phosphate buffer (pH 1.679), significant amounts of adipic acid was found, while only trace levels of oligomers and 1,4-butanediol were detected. This was explained by a further hydrolysis of oligomers to monomers and oxidation of 1,4-butanediol. The formation of adipic acid was more affected by pH of the aging media than by different aging temperatures, while the inverse relationship was seen for mass loss and water absorption. Strong influence of temperature on migration and degradation of plasticizer was also seen when PVC plasticized with poly(caprolactone-carbonate) was aged in water and phosphate buffer at different temperatures.<sup>26,27</sup> At 37°C, practically no migration of plasticizer was detected after 98 days, while at an aging temperature of 100°C, blends were rapidly almost depleted of plasticizer.

The literature mainly reports of blends of PVC with different linear polyesters. However, in 1967,

Huber et al.<sup>20</sup> patented a medium degree branched aliphatic polyester, based on dicarboxylic acids, monocarboxylic acids, glycols, and trihydric alcohols such as glycerin, trimethylol propane, trimethylol butane, and trimethylol ethane.<sup>20</sup> They reported of better compatibility with PVC, improved thermal stability, and reduced migration of plasticizer to styrene-butadiene rubber (SBR). Recently, Choi and Kwak reported on the use of hyperbranched poly( $\epsilon$ -caprolactone)<sup>28</sup> and another highly branched, patented polyester<sup>29</sup> as plasticizers. Plasticizing efficiency, measured by the shifting of  $T_g$  and tensile elongation, was found to be similar to that of DEHP and favored by shorter linear segments and more branching.<sup>28,29</sup> Migration of the hyperbranched plasticizer to *n*-hexane, unplasticized PVC, and poly(ethylene terephthalate) was reduced compared to DEHP. We have in an earlier study shown improved mechanical properties and compatibility for blends of PVC with slightly branched PBA.<sup>30</sup> The aim of this work was to evaluate if the stability of polyester plasticizers and their migration resistance is improved by low degree of branching and by modification of end-group functionality.

## EXPERIMENTAL

### Materials

Flexible PVC films used in migration tests were obtained by solvent casting PVC with nine different plasticizers. Seven aliphatic polyesters [three linear and four branched poly(butylene adipate)s (PBAs)] and two phthalate esters [bis(2-ethylhexyl)phthalate (DEHP) and dioctyl phthalate (DOP)] (Table I) were used as plasticizers. Each plasticizer was added in a 40 wt % concentration. Synthesis and characterization of polyesters as well as solution casting procedure were described in an earlier study.<sup>30</sup> The film thicknesses were ~50–60  $\mu$ m.

**TABLE I**  
Material Characteristics of Polyesters and Phthalate Esters Used as Plasticizers in PVC Films

Plasticizer <sup>a</sup>	Monomers <sup>b</sup>	Number-average molar mass (g/mol)	Weight-average molar mass (g/mol)	Degree of branching
L1-AA	AA and BD	2,300	3,300	0
L2-AA	AA and BD	4,100	6,100	0
L3-DMA	DMA and BD	7,800	14,500	0
B1-AA	AA and BD	4,200	6,900	0.8
B2-DMA	DMA and BD	5,000	8,000	1.8
B3-AA	AA and BD	5,400	8,800	0.4
B4-DMA	DMA and BD	9,700	17,500	0.2
DOP		390	390	0
DEHP		390	390	0

<sup>a</sup> L1–L3, linear PBA; B1–B4, branched PBA; AA, synthesized from adipic acid; DMA, synthesized from dimethyl ester of adipic acid.

<sup>b</sup> Generic term for adipic acid (AA), dimethyl ester of adipic acid (DMA), and 1,4-butanediol (BD).

## Hydrolysis

PVC/PBA films (0.25 g) containing 40 wt % PBA was aged in 20 mL glass vials containing 3.5 mL of water (HPLC grade from Fluka, Buchs, Switzerland). The vials were sealed by 5 M/1 Teflon white-faced white silicone septas (20 mm diameter and 0.125 in. thick) from Supelco (PA, USA). All films were aged at 37°C for 10 weeks.

## Solid phase extraction procedure

Prior to identification of degradation products by gas chromatography–mass spectrometry, extraction of formed hydrolysis products from the sample solution was carried out according to an earlier developed SPE method.<sup>31</sup> The ISOLUTE<sup>®</sup> ENV+ column was conditioned with 1 mL of methanol and equilibrated with 1 mL of water (pH < 2). The pKa values of our expected analytes are 14.5 for 1,4-butanediol and 4.41 and 5.41 for the first and second hydroxyl group in adipic acid. The pH of the sample solution was thus adjusted to pH < 2 with concentrated HCl to ensure protonation of carboxylic acids. In addition to HCl, 1.5 µL of standard solution (1,5-pentanediol and glutaric acid, 1 g of each/10 mL water) was added to 3 mL of sample solution before it was applied to the SPE column. After passing through the sample, the column was dried with compressed air, applied through a column-adapted syringe. Degradation products were eluted from the solid phase with 1 mL of acidic methanol (0.1% HCl). The acidic methanol methylized the dicarboxylic acids to methyl esters of respective acid, which improved the behavior in GC column. To quantify the amount of degradation products formed, calibration solutions were prepared by dissolving known amounts of the monomers in water containing internal standards (glutaric acid and 1,5-pentanediol). Extraction from the calibration solutions was done by the same SPE method described above. Calibration curves were then prepared for each compound to calculate the amounts in unknown samples.

## Gas chromatography–mass spectrometry

Identification and quantification of extracted degradation products was done by a ThermoFinnigan GCQ (San José, CA). The column used was a wall-coated open tubular (WCOT)-fused silica CP-WAX 52CB column (30 m × 0.25 mm I.D., D.F. 0.25 µm) from Varian (Lake Forest, CA). Helium of scientific grade purity from AGA (Stockholm, Sweden) was used as carrier gas at the constant velocity of 40 cm/s (the electronic pressure control, EPC, of the GC was used to control the flow velocity). The initial oven temperature was 40°C, which was held for 1 min. The oven was heated to 250°C at the heating rate 10°C/min, and held at 250°C for 20 min. Electron impact mode, EI, was used

with an electron energy of 70 eV. The mass-range scanned was 35–500 *m/z* and the ion source and transfer line temperatures were 180°C and 250°C, respectively. The injector temperature was set to 250°C. One microliter of sample was injected in splitless injection mode and three blanks were run between each sample by injection of clean methanol. Identification of monomeric degradation products was confirmed by comparing their retention times and mass spectra to those of corresponding standard compounds. Oligomeric products were identified by their EI mass spectra, in single MS, and their quasi-molecular ions obtained in chemical ionization mode, CI, with methane as a reagent gas.

## Water absorption and mass loss

Water absorption of aged films was measured by weighting the cautiously wiped films before letting them dry in desiccator until constant weight. After the films were dried to constant weight, mass loss was calculated. Water absorption was calculated from the dry weight according to eq. (1).

$$\text{Water absorption (\%)} = \left[ \frac{\text{Wet weight} - \text{Dry weight}}{\text{Dry weight}} \right] \times 100 \quad (1)$$

## Fourier transform infrared spectroscopy

Infrared spectra of synthesized polyesters and solution-cast films were recorded on a PerkinElmer Spectrum 2000 FTIR spectrometer (Norwalk, CT) equipped with a single reflection-attenuated total reflectance (ATR) accessory (golden gate) from Graseby Specac (Kent, UK).

## Tensile testing

Tensile testing of solution-cast films was conducted on an Instron 5566, equipped with pneumatic grips and Instron series IX software (Bristol, UK). Five dry samples of uniform shape (80 × 5 mm<sup>2</sup>) were cut using a EP 04/80 × 5 mm<sup>2</sup> specimen cutter from Elastocon AB, Sweden, and drawn to break from an initial grip separation of 25 mm, at a crosshead speed of 50 mm/min and with a load cell of 0.1 kN. The sample thickness was measured using a digital thickness gauge (Mitutoyo micrometer) and elongation at break was calculated from grip separation. ASTM standard D 882-02 was followed with exception of conditioning procedures. Tensile modulus of elasticity was not measured due to insufficient sample lengths.

## Differential scanning calorimetry

DSC analyses were performed on a Mettler-Toledo DSC 820 under nitrogen atmosphere. Five to ten

milligrams of dried polymer or polymer film was encapsulated in a 40  $\mu\text{L}$  aluminum cap without pin. Samples were under a nitrogen gas flow of 80 mL/min, heated from 25 to 80°C at a rate of 5°C/min. Thereafter the samples were cooled from 80 to 25°C at a rate of 5°C/min, from 25°C to -50°C at a rate of 1°C/min, and from -50°C to -70°C at a rate of 0.5°C/min to ensure controlled crystallization. The samples were held isothermally at -70°C for 10 min before being heated from -70°C to 120°C at a rate of 5°C/min. Samples containing pure PVC were heated to 120°C also in the first heating cycle.

### Multivariate data analysis

Principal component analysis (PCA) was performed using software program SIMCA P 10.0.2.0 from Umetrics AB (Umeå, Sweden). PCA models were created using data-covering material and mechanical properties as well as migration behavior. Computational options used were: scaling to unit variance and mean centering of data, 95% confidence level, automatic fit of principal components, cross-validation and eigenvalues were used to validate the model. Definitions used in cross-validation:

$R^2X$  = The fraction of sum of squares of the data table X explained by the current principal component. This value is often called the explained variance and estimates the goodness of fit.

$Q^2X$  = The fraction of the total variation of the data table X that can be predicted by the current principal component. This value is often

called the predicted variance and estimates the goodness of prediction.

Loading plots = Plots describing the relationship among different variables (properties) and their influence on the model.

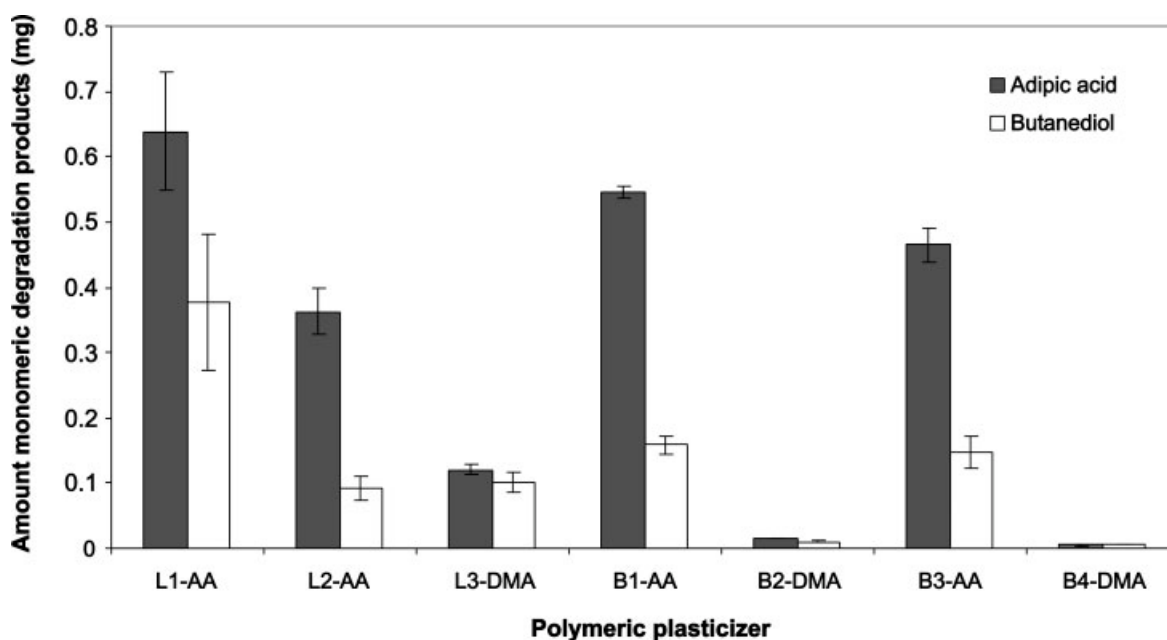
Score plots = Plots describing the relationship among observations and their placement in the model space.

## RESULTS AND DISCUSSION

Good miscibility with PVC makes aliphatic polyesters an interesting alternative as substitute for phthalate ester plasticizers. A drawback is the possible formation and migration of low molar mass compounds due to hydrolysis of the polyesters. Several PBAs were solution-cast with PVC, to elucidate how different molar mass, end-groups, and degrees of branching influence the sensitivity toward hydrolysis and the migration process. Dry films were aged in water and analyzed with respect to mass loss, water absorption, and migration of monomeric hydrolysis products.

### Migration of hydrolysis products from PVC/PBA films

The low molar mass compounds migrating from PVC/PBA films aged in water at 37°C for 10 weeks were extracted by solid-phase extraction and identified by subsequent GC-MS analysis. Considerable differences in the amount of monomeric degradation products were seen between the different materials (Fig. 1).



**Figure 1** Amount (mg) of adipic acid and 1,4-butanediol migrating from PVC/PBA films after aging in water at 37°C for 10 weeks.



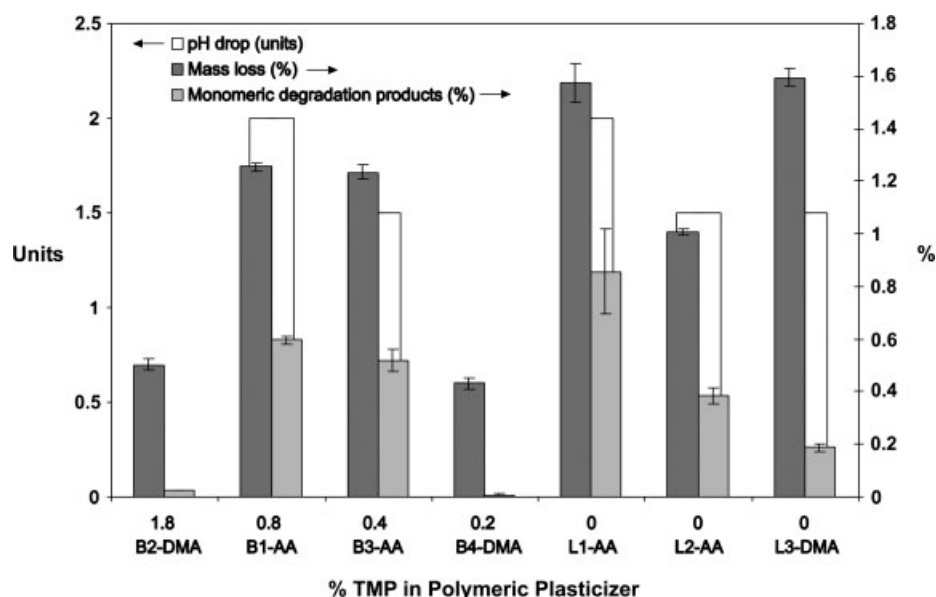
Significantly lower levels of monomeric degradation products migrated from the films plasticized with polyesters synthesized from dimethyl ester of adipic acid (DMA) compared to polyesters synthesized from adipic acid (AA). Although the effect was most important for the branched polyesters, the linear polyester synthesized from DMA also showed lower levels of monomeric degradation products compared to the linear polyesters synthesized from adipic acid. This indicates that methyl ester end-groups have a stabilizing effect toward hydrolysis, which in turn reduces the amount of monomeric degradation products released from the material. The catalytic effect of carboxylic acid end-groups on ester-hydrolysis and the hydrolysis-inhibiting results of end-capping has been shown in many studies on polyester hydrolysis.<sup>32–37</sup> Reduced rate of chain-scission by partial ethoxylation of poly(caprolactone) was seen by Pitt and Gu in 1987<sup>34</sup> and improved hydrolytic stability was obtained when the amount of carboxylic end-groups was reduced in a poly(butylene terephthalate) polymer.<sup>35</sup> Increased hydrolysis rate of star-shaped PLA<sup>36</sup> was seen when the arms were functionalized with carboxylic end-groups compared to  $-OH$ ,  $-Cl$ , and  $-NH_2$  end-groups. Hydroxyl end-groups were the second best catalyst for the hydrolysis reaction and degradation rate increased with increasing number of arms.<sup>36</sup> In accordance with an earlier study on poly(lactide-co-glycolide),<sup>37</sup> our results show that although a trend of somewhat increased hydrolysis rate can be seen for plasticizers with lower molar mass, i.e., L1-AA, the nature of end-groups was far more important to the formation of low molar mass products.

When polyesters synthesized from adipic acid were blended with PVC, somewhat higher amounts of adipic acid compared to 1,4-butanediol were detected. However, when calculated in moles, the largest difference only amounts to 4 mol % of the total amount of end-groups present in the polyester at the beginning of aging. This small difference in the amount adipic acid compared to 1,4-butanediol is only present in samples polymerized from adipic acid and it is, thus, explained by a somewhat higher hydrolysis rate of the adipic acid chain-ends due to auto-catalysis.

Low molar mass oligomers of PBA were also detected in the GC-MS chromatograms. The relative amounts of oligomeric products from the different blends were in good agreement with the amount of monomeric products. In blends plasticized with polyesters synthesized from DMA, significantly lower amounts of monomeric and oligomeric hydrolysis products were detected compared to blends plasticized with polyesters synthesized from adipic acid.

#### Mass loss and water absorption during aging

Paralleled to following the formation of low molar mass products, migration and hydrolysis were also followed by measuring mass loss, water absorption, and pH-changes in the aging media. The amounts of degradation products migrating from films plasticized with B2-DMA or B4-DMA during 10 weeks of aging was not high enough to affect the pH of the aging medium (Fig. 2). For films plasticized with other polymeric plasticizers the pH of the water decreased by 1.5–2.0 units during the aging period. Mass loss was



**Figure 2** Weight-percent of monomeric degradation products migrating from PVC/PBA films after aging in water at 37°C for 10 weeks, compared to mass loss and pH-changes of the aging medium. (Weight-percent of monomeric degradation products were calculated as detected amount/amount theoretically possible.)

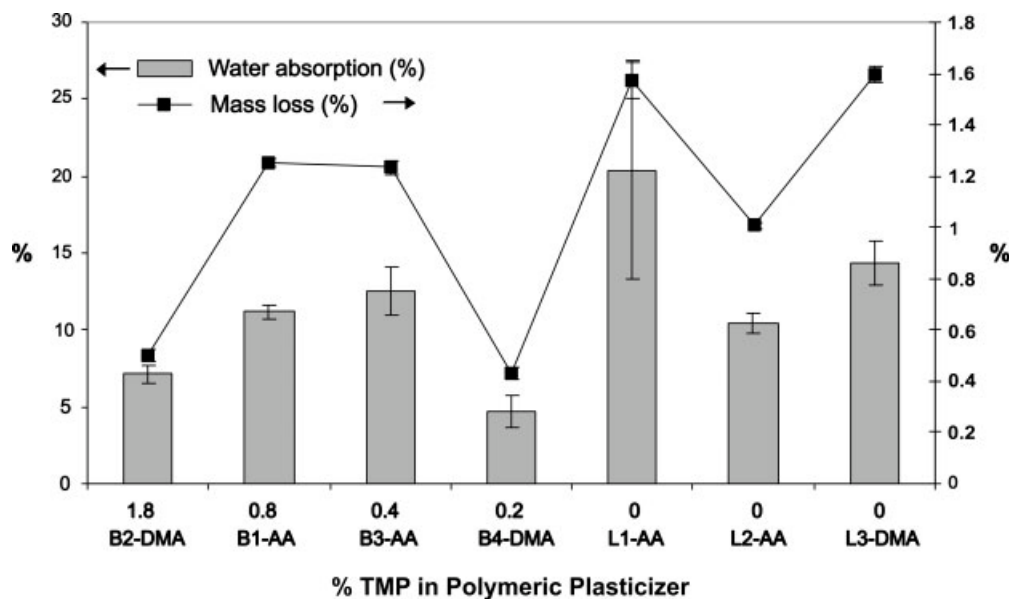


Figure 3 Mass loss and water absorption of PVC/PBA films after aging in water at 37°C for 10 weeks.

generally very low (0.5–1.6%) and was in good agreement with the amount of monomeric products detected (Fig. 2).

Comparison of the amount of monomeric products and the overall mass loss of aged films showed that the monomeric species corresponded to ~50% (38–54%) of the mass loss for films plasticized with polyesters synthesized from adipic acid (i.e., L1-AA, L2-AA, B1-AA, and B3-AA). However, for films plasticized with polyesters synthesized from DMA (i.e., L3-DMA, B2-DMA and B4-DMA), only ~10% (2–12%) of the mass loss was due to formation of monomers, which additionally confirms the hydrolysis-protecting function of the methyl ester end-groups. The mass loss of the film plasticized with a linear DMA-based polyester (L3-DMA) was similar to the mass loss of films plasticized with linear adipic acid-based polyesters, and a reduction in the total amount of migrating degradation products was, thus, obtained by combining a branched polymer structure and hydrolysis-

protecting end-groups. Figure 3 shows the good agreement between water absorption and mass loss during the hydrolysis.

#### Correlation of the material properties and migration behavior

Mechanical and material properties of synthesized polyesters and solution-cast films were characterized by SEC, NMR, FTIR, DSC, and tensile testing. The results of these analyses were more thoroughly reported in an earlier study,<sup>30</sup> but an overview of the results is shown in Tables I and II.

The migration test showed lower migration rate and reduced mass loss for films plasticized with branched polyesters synthesized from DMA, e.g., B2-DMA and B4-DMA, compared to films plasticized with the other polyesters. The same films also showed higher ductility and superior miscibility between polyester and PVC in tensile testing and FTIR analyses. Miscibility of

TABLE II  
Overview of Mechanical Properties of PVC/PBA Films

Plasticizer	Strain at break (%)	Stress at break (MPa)	Degree of crystallinity (%; first heating)	Mixed surface spectra (FTIR)	Carbonyl shift (cm <sup>-1</sup> , absolute value)
L1-AA	507	24.6	24	No	1
L2-AA	523	23.6	11	No	2
L3-DMA	504	23.2	3	No	2
B1-AA	560	23.7	5	No	2
B2-DMA	617	29.4	4	Yes	5
B3-AA	508	21.1	7	No	2
B4-DMA	538	25.6	2	Yes	4
DOP	562	17		Yes	3
DEHP	533	17.6		Yes	3

**TABLE III**  
**Properties and Abbreviations Used in PCA Models**

Blend property	Variable abbreviation in PCA
Synthesized from DMA	DMA
Strain at break	Strain
Stress at break	Stress
Carbonyl absorption shift	Miscibility
Mixed surface spectra	Surface
Degree of crystallinity	Crystallinity
Amount of monomeric degradation products	Migration
Mass loss	Mass loss
Water absorption	Water absorption

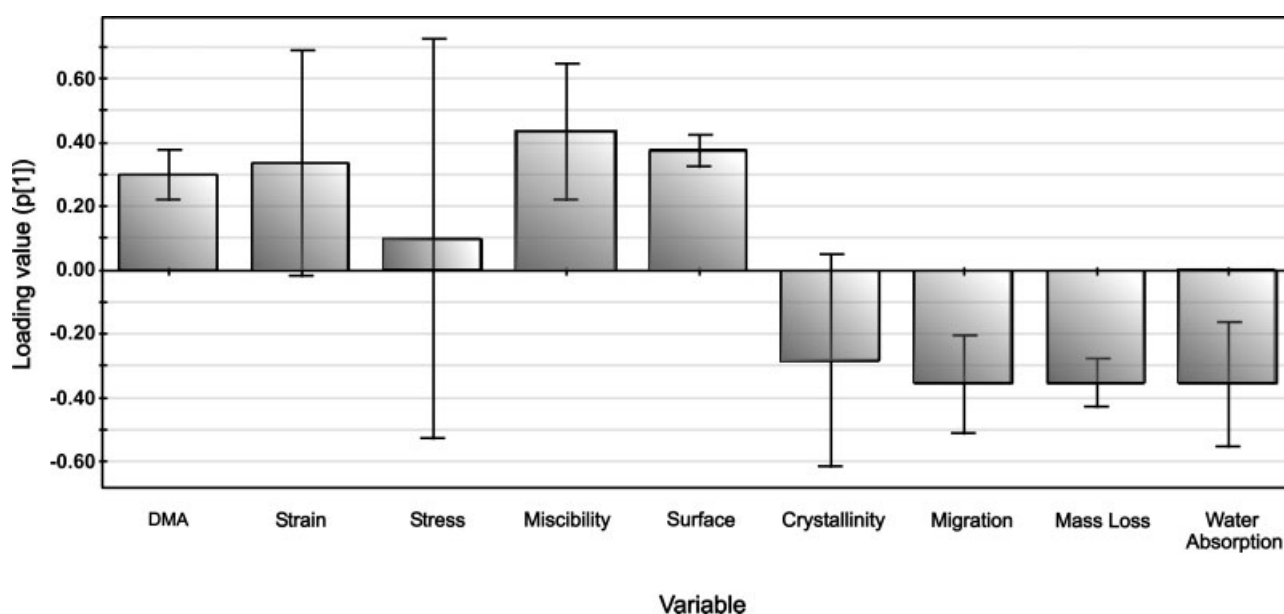
PVC and polyesters has in several studies been shown to cause a shift in the carbonyl group stretch absorption band in FTIR.<sup>38,39</sup> This shift is caused by intermolecular interactions between PVC and polyester. In films plasticized with branched polyesters synthesized from DMA, FTIR spectra of the surface contained absorption band characteristics of both PVC and the polyester, and a greater shifting of the carbonyl group absorption band, which indicates a higher extent of intermolecular interactions between PVC and the polyester. In films with lower miscibility between the polyester and PVC, e.g., films plasticized with L1-AA, surface segregation caused enrichment of the polyester at the surface, and in turn facilitated water absorption, since PBA is a more hydrophilic polymer than PVC. Enrichment of the polyester at the surface also made the polyester more accessible to the water and thereby more vulnerable to hydrolysis.

As seen in Table II, the use of a branched plasticizer with methyl end-groups also resulted in lower degree of crystallinity. The films with a somewhat higher degree of crystallinity, i.e., L1-AA, exhibited higher water absorption and hence increased mass loss and migration of low molar mass products compared to samples with a lower degree of crystallinity e.g., B2-DMA and B4-DMA. This is in good correlation with superior miscibility between PVC and the branched polyesters with methyl end-groups, and an indication that a higher concentration of polyester at the surface has a greater impact on the sensitivity toward hydrolysis than an increased degree of crystallinity.

### Multivariate data analysis

Multivariate data analysis was used to evaluate the different results obtained by tensile testing, FTIR, DSC, migration observations, and material characteristics to find out if the blends divided themselves according to any specific pattern when mechanical/material properties and migration behavior were considered simultaneously. In an earlier study,<sup>30</sup> tensile testing and FTIR of PVC/PBA films containing 20, 40, and 60 wt % PBA showed that superior mechanical properties and miscibility were obtained when the polyester content in films was 40 wt %. Based on that study, 40 wt % was the only concentration chosen to be included in this study.

A first PCA model was fitted to the properties listed in Table III. PCA-model 1 was fitted with one principal component and cross-validation gave the explained variance  $R^2 = 0.637$  and predicted variance



**Figure 4** Loading column plot of PCA-model 1 including mechanical and material properties, and migration behavior of PVC/PBA films plasticized with 40 wt % plasticizer. The variable stress is poorly described by the model, as can be seen by the large standard deviation, and of little importance to the model, indicated by the low loading-value.

$Q^2 = 0.311$ . The model's eigenvalue was 5.74 but the low  $R^2$  and  $Q^2$  values of PCA-model 1 indicate a badly fitted model to the data. Analysis of the loading plot (Fig. 4) shows that the variable stress is both very poorly described by the model and of little importance to the observations placement in the score plots.

As the variable stress was both poorly explained by the model and of little importance to the placement of observations in the score plots, this variable was excluded and a second PCA-model was fitted to the other properties listed in Table III. PCA-model 2 was also fitted with one principal component but cross-validation now showed an explained variance  $R^2 = 0.727$  and a predicted variance  $Q^2 = 0.516$ . The model's eigenvalue was 5.82. These values signify a well-fitted model and trends indicated by this model agree with trends seen in PCA-model 1, which confirms the low importance of the stress variable.

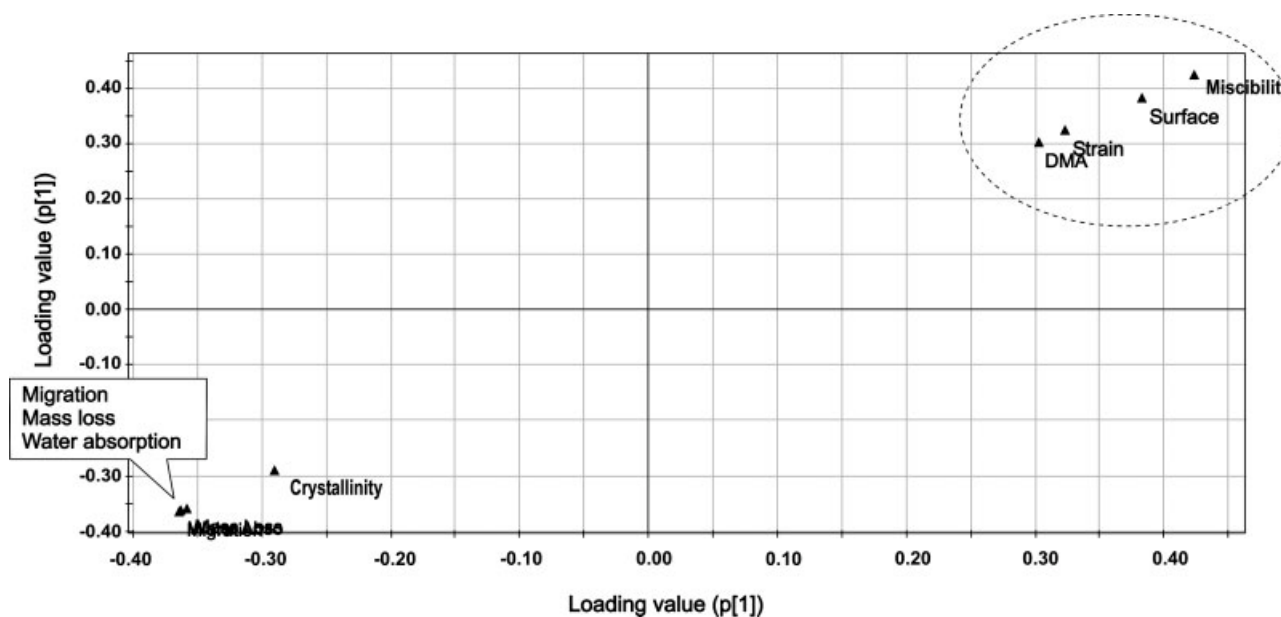
Analysis of the loading plot of PCA-model 2 shows that the variables are grouped in two groups (Fig. 5). The first group includes the variables DMA, strain, miscibility, and surface character, the other group contains the variables crystallinity, migration, mass loss, and water absorption. Variables within each group are positively correlated but the two groups are negatively correlated, that is, when the values in one group increase, the values in the other group decrease.

The score plot of PCA-model 2 shows that the observations are also grouped in two groups (Fig. 6). Observations B2-DMA, B4-DMA, DOP, and DEHP have similar properties, while observations L1-AA, L2-AA,

L3-DMA, B1-AA, and B3-DMA have the opposite properties. No strong or moderate outliers were found in the analysis.

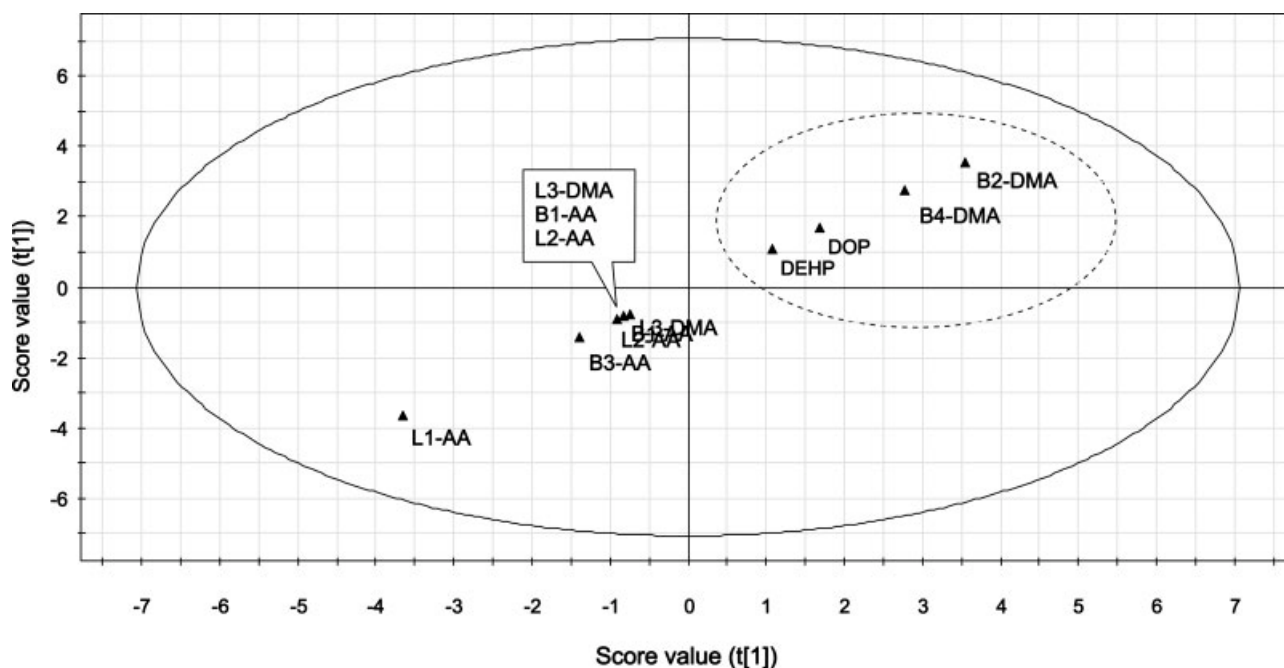
From correlating the loading and score plots of PCA-model 2 (in Figs. 5 and 6, respectively), we can see that observations B2-DMA, B4-DMA, DOP, and DEHP (marked by a dashed ellipse in Fig. 6) have high values for DMA, strain, miscibility, and surface character (also marked by a dashed ellipse in Fig. 5), and low values for crystallinity, migration, mass loss, and water absorption. These observations thus have an attractive combination of properties for a flexible film material. The higher scores for B2-DMA and B4-DMA (i.e., a placement farther from origin in Fig. 6) than for DOP and DEHP indicate an even better match of the properties desirable for flexible PVC-materials to films plasticized with methyl ester-terminated, branched polymeric plasticizers compared to films plasticized with traditional phthalate plasticizers.

It is clear from the PCA that blends plasticized with B2-DMA and B4-DMA stand out from the rest of the blends plasticized with polyesters; migration and mass loss is very low but also mechanical and material properties are similar to those of blends plasticized with traditional low molar mass plasticizers DOP and DEHP. Thus, to learn how to design a polyester that fulfills the desired properties of a plasticizer for PVC, characteristic differences between B2-DMA and B4-DMA contra L1-AA, L2-AA, L3-DMA, B1-AA, and B3-AA were studied and concluded as earlier; they are the only branched polyesters synthesized from DMA. The combined effect of these two characteristics is thus that



**Figure 5** Two-dimensional loading scatter plot of PCA-model 2 including mechanical and material properties, and migration behavior of PVC/PBA films plasticized with 40 wt % plasticizer. Dashed ellipse: properties that are positively correlated to observations B2-DMA, B4-DMA, DOP, and DEHP (also marked by a dashed ellipse) in Figure 6. Variables placed in the opposite corner of the figure are negatively correlated to the variables inside the dashed ellipse.





**Figure 6** Two-dimensional score scatter plot of PCA-model 2 including the different samples of PVC/PBA films plasticized with 40 wt % plasticizer. Continuous ellipse: Hotelling's  $T^2$  (0.05), dashed ellipse: observations with favorable properties.

synthesizing the polyester from DMA rather than from adipic acid provides the polyester with hydrolysis-protecting methyl ester end-groups, and the branched structure improves the miscibility between PVC and the polyester. Improved miscibility both inhibits water absorption, and in that way reduces the possibilities for hydrolysis additionally, and improves the mechanical properties of the material.

### CONCLUSIONS

Methyl ester end-groups in poly(butylene adipate) (PBA) protected the polymeric plasticizer from hydrolysis and reduced the migration of monomeric degradation products from PVC/PBA films during contact with aqueous solutions. Introducing branches in the polyester structure increased the miscibility between PVC and the polyester, resulting in improved mechanical properties of the blend and less water absorption upon aging in water. The combination of branching and protective methyl ester end-groups resulted in migration resistant polymeric plasticizer with strongly reduced hydrolysis rate, negligible migration of monomeric degradation products, and lower mass loss and water absorption compared to linear polyester plasticizers.

Professor Ann-Christine Albertsson and Dr. Mikael Gröning are acknowledged for valuable discussions during this work. Lina Emilsson and Carl Brunius are thanked for synthesizing the PBA polymers.

### References

- Rahman, M.; Brazel, C. S. *Prog Polym Sci* 2004, 29, 1223.
- Jaeger, R. J.; Rubin, R. J. *Science (Wash.)* 1970, 170, 460.
- Latini, G.; De Felice, C.; Verrotti, A. *Reprod Toxicol* 2004, 19, 27.
- Ticker, J. A.; Schettler, T.; Guidotti, T.; McCally, M.; Rossi, M. *Am J Ind Med* 2001, 39, 100.
- Hill, S. S.; Shaw, B. R.; Wu, A. H. B. *Clin Chim Acta* 2001, 304, 1.
- Kleinsasser, N. H.; Harreus, U. A.; Kastenbauer, E. R.; Wallner, B. C.; Sassen, A. W.; Staudenmaier, R.; Rettenmeier, A. W. *Toxicol Lett* 2004, 148, 83.
- Cederberg, I. Information from KEMI; Swedish Chemicals Inspectorate: Sundbyberg, Sweden, 2005; p 13.
- Postle, M. C. C.; van den Berg, N.; Sanderson, T. The Availability of Substitutes for Soft PVC Containing Phthalates in Certain Toys and Childcare Articles. ETD/99/502498. European Commission Directorate-General Enterprise 2000.
- Czuba, L. *Med Device Diagn Ind* 1999.
- Lakshmi, S.; Jayakrishnan, A. *Artif Organs* 1998, 22, 222.
- Messori, M.; Toselli, M.; Pilati, F.; Fabbri, E.; Fabbri, P.; Pasquali, L.; Nannarone, S. *Polymer* 2004, 45, 805.
- Jayakrishnan, A.; Lakshmi, S. *Nature* 1998, 396, 638.
- Ito, R.; Seshimo, F.; Haishima, Y.; Hasegawa, C.; Isama, K.; Yagami, T.; Nakahashi, K.; Yamazaki, H.; Inoue, K.; Yoshimura, Y.; Saito, K.; Tsuchiya, T.; Nakazawa, H. *Int J Pharmacol* 2005, 303, 104.
- Bourdeaux, D.; Sautou-Miranda, V.; Bagel-Boithias, S.; Boyer, A.; Chopineau, J. *J Pharm Biomed* 2004, 35, 57.
- Di Landro, L.; Capone, C.; Inzoli, F.; Malacari, P. E. *J Vinyl Addit Technol* 2005, 11, 111.
- Shah, B. L.; Shertukde, V. V. *J Appl Polym Sci* 2003, 90, 3278.
- Han, Y. K.; Um, J. W.; Im, S. S.; Kim, B. C. *J Polym Sci Part A: Polym Chem* 2001, 39, 2143.
- Brady, J. M.; Cruz-Ramos, C. A. In *Polymer Blends*; Paul, D. R., Bucknall, C. B., Eds.; Wiley: New York, 2000.
- Bohrer, G. J. U.S. Pat. 2,838,428 (1958).

20. Huber, C. F.; Foulks, H. C. J.; Aylesworth, R. D. U.S. Pat. 3,331,802 (1967).
21. Prud'homme, R. E. *Polym Eng Sci* 1982, 22, 90.
22. Ziska, J. J.; Barlow, J. W.; Paul, D. R. *Polymer* 1981, 22, 918.
23. Coleman, M. M.; Zarian, J. *J Polym Sci Part B: Polym Phys* 1979, 17, 837.
24. Castle, L.; Mercer, A. J.; Gilbert, J. *Food Addit Contam* 1991, 8, 565.
25. Wang, Q.; Storm, B. K. *Macromol Symp* 2005, 225, 191.
26. Hakkarainen, M. *Polym Degrad Stab* 2003, 80, 451.
27. Hakkarainen, M. *J Chromatogr A* 2003, 1010, 9.
28. Choi, J.; Kwak, S.-Y. *PMSE Prepr* 2004, 90, 449.
29. Kwak, S.-Y.; Choi, J.-S. U.S. Pat. 6,747,092 (2004).
30. Lindstrom, A.; Hakkarainen, M. *J Appl Polym Sci* 2006, 100, 2180.
31. Lindstrom, A.; Albertsson, A.-C.; Hakkarainen, M. *J Chromatogr A* 2004, 1022, 171.
32. Brown, D. W.; Lowry, R. E.; Smith, L. E. *Macromolecules* 1980, 13, 248.
33. Huffman, K. R.; Casey, D. J. *J Polym Sci Part A: Polym Chem* 1939, 1985, 23.
34. Pitt, C. G.; Gu, Z. W. *J Controlled Release* 1987, 4, 283.
35. Gallucci, R. R.; Dellacolella, B. A.; Hamilton, D. G. *Plast Eng* 1994, 50, 51.
36. Lee, S.-H.; Kim, S. H.; Han, Y.-K.; Kim, Y. H. *J Polym Sci Part A: Polym Chem* 2001, 39, 973.
37. Tracy, M. A.; Ward, K. L.; Firouzabadian, L.; Wang, Y.; Dong, N.; Qian, R.; Zhang, Y. *Biomaterials* 1999, 20, 1057.
38. Garton, A.; Aubin, M.; Prud'homme, R. E. *J Polym Sci Polym Lett Ed* 1983, 21, 45.
39. Varnell, D. F.; Moskala, E. J.; Painter, P. C.; Coleman, M. M. *Polym Eng Sci* 1983, 23, 658.