Biomacromolecules **2007,** *8, 1187*−*1194*

Designed Chain Architecture for Enhanced Migration Resistance and Property Preservation in Poly(vinyl chloride)/ Polyester Blends

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Received January 1, 2007; Revised Manuscript Received January 25, 2007

Blends of poly(vinyl chloride) (PVC) and poly(butylene adipate) (PBA) with varying degrees of branching were analyzed with respect to migration resistance during aging in water, preservation of material properties, and thermal stability. Gas chromatography−mass spectrometry, water absorption, weight loss, thermogravimetric analysis, Fourier transform infrared spectroscopy, contact angle, tensile testing, and differential scanning calorimetry were used to analyze the blends before and after aging in water for 6 weeks. Films plasticized with slightly branched polyester maintained their material and mechanical properties best during aging. High degree of branching was accompanied by poor miscibility, increased hydrophilicity, and polydispersity, and highly branched PBA was not favorable as a plasticizer. Strong intermolecular interactions reduced the water absorption and increased the migration resistance of the blends. Polymeric plasticizers with no, low, or moderate degree of branching improved the thermal stability of films compared to films plasticized with a traditional phthalate plasticizer. Proper design of plasticizer architecture led, thus, to improved migration resistance, long-term properties, and thermal stability in PVC/polyester blends.

Introduction

Soft plastic articles have been plasticized with low molecular weight phthalate plasticizers since the 1920s.[1] As a result of their low molecular weight, phthalate plasticizers have low permanence in the material and they have been found all around in the environment and in both animals and humans.[2−4] When released to indoor air, they are accumulated in household dust[5,6] and transfer to humans can be trough inhalation, ingestion, or dermal contact.[5] When released to marine environments, they are absorbed by organic matter and passed on in the marine food chain.[7] Certain environments are harsher than others. When plasticized PVC is used in medical devices and toys, the extraction of low molecular weight additives is accelerated by the aggressive nature of biological fluids, for example, saliva and gastric juice. The loss of plasticizers affects the long-term properties of the material and the migration of harmful substances to the environment and to humans[3,8−10] is not in concurrence with a sustainable society. New legislation[11,12] forbidding the use of some of the most common phthalate plasticizers in toys and childcare articles within the European Union calls for a continued development of safe and well-performing alternative plasticizers that can be used in flexible PVC formulations.

One alternative studied is the use of aliphatic polyesters as nontoxic polymeric plasticizers.[13−17] The phase behavior between two polymers is a balance between interpolymeric interactions and self-association.[18] Specific interactions between polymer chains can compensate the low combinatorial entropy change naturally associated with polymer mixing and induce miscibility in a polymer blend.[19] By choosing suitable components that can form intermolecular interactions, balancing the right composition, and controlling the molecular weight and architecture of the polymers in the blend, material properties like migration resistance and surface enrichment can be controlled.[20−22]

The more spherical structure of hyperbranched polymers (HBPs) compared to linear polymers reduces the number of chain entanglements between chains,[23] and blends of linear and hyperbranched polymers have shown lower melt viscocity[24] and improved processability compared to blends containing only linear polymers.[16] Hyperbranched polymers have a high density of possible active centers because functional groups can be placed both at the large number of chain ends and throughout the structure. This greatly affects properties such as glass transition temperature, miscibility with other polymers, and solubility.[24−26] When mixed with a linear resin, branched or hyperbranched polyester would increase the mobility of the system compared to a system containing a linear polymer. The high molecular weight and bulky structure of the branched polymer would also significantly reduce its volatility and diffusivity compared to low molecular weight plasticizers.

The literature mainly reports on blends of PVC with different linear polyesters, and only a few studies have been reported on the mixing of branched or highly branched polyesters with PVC.[27−29] A highly branched polyester plasticizer based on dicarboxylic acids, monocarbocylic acids, diols, and triols was patented by Huber et al.[27] in 1967. When blended with PVC, the polyester showed good miscibility and the migration of plasticizer to styrene−butadiene rubber (SBR) was significantly reduced. Hyperbranched poly(ϵ-caprolactone)[29] and a series of highly branched, patented polyesters[28] similar to hyperbranched poly(ϵ-caprolactone) were reported by Choi and Kwak in 2004.[28,29] Blends of these polyesters with PVC also showed good plasticizing efficiency, and the migration of plasticizer to *n*-hexane, unplasticized PVC, and poly(ethylene terephthalate) was reduced compared to bis(2-ethylhexyl) phthalate (DEHP).

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10.1021/bm070001k CCC: $37.00

Table 1. Polyesters Used as Polymeric Plasticizers for PVC

polyester	DMA/BD/BT (molar ratio)	$\overline{M}_n$ (g/mol)	$\overline{M}_w$ (g/mol)	PDI	branching frequency	Mark−Houwink-α	T_m (°C)	w_c (%)
PBA-L	1.00/1.00/0.00	2400	4700	2.0	0.00	0.557	56	83
PBA-B1	1.00/0.96/0.05	2100	5000	2.3	0.19	0.467	51	66
PBA-B2	1.00/0.75/0.25	1000	3300	3.2	0.54	0.414	41	19
PBA-B3	1.00/0.00/1.00	700	6700	9.6	1.23	0.305		

The migration of polymeric plasticizers or their migration products from flexible PVC products plasticized with linear polymers has been reported in a few studies.[16,30−35] The release of monomers and oligomers from PVC plasticized with linear poly(butylene adipate) to water[32,35] and olive oil[31] suggests that the concept of polymeric plasticizers for PVC needs to be further developed. We believe that introducing branches in the plasticizer structure could be an effective way to reduce the amount of low molecular weight species released during use and at the same time obtain desirable material properties. We have in earlier studies investigated the release profile of PVC/poly(caprolactone-carbonate) blends[33] and blends of PVC and poly(butylene adipate) with low degree of branching.[34,35] During this study four poly(butylene adipate)s (PBA), the structures varying from linear to hyperbranched, were synthesized and solution-cast with PVC to investigate the effect of miscibility and chain architecture on migration resistance and preservation of material properties during aging in water. In addition, the thermal stabilization effect of polyester plasticizers was also evaluated. As far as we know, there are no other studies that have evaluated the effect of architecture and such a wide range of branching on the long-term properties and migration resistance of PVC/polyester blends in aqueous environments.

Experimental Section

Materials. Solution-cast films of PVC and four aliphatic polyesters were prepared by dissolving 2 g of polymer in 80 mL of tetrahydrofuran (THF). The dissolved blend was cast in clean Petri dishes (with lids) and dried at ambient pressure and room temperature for 3 days and in a vacuum desiccator for an additional 3 days. The dry films were approximately 60 μm thick and contained 20 or 40 wt % polyester. Linear and branched polyesters used in the solution cast blends were prepared by polycondensation of 1,4-butanediol (BD) (≥99%), 1,2,4-butanetriol (BT) (96%), and dimethyl ester of adipic acid (DMA) (≥99%) according to the molar ratios reported in Table 1. Dibutyltin(IV) oxide [$(n\text{-Bu})_2\text{SnO}$] (98%) was used as a catalyst, tetrahydrofuran (99.8%) and methanol (≥99.8%) were used to dissolve the polyesters, and diethyl ether (99%) was used for precipitation. The details of the syntheses are described in an earlier paper.[36] The different poly(butylene adipate)s used as polymeric plasticizers in this study varied in average molecular weight, molecular weight distribution, degree of branching, melting temperature, and degree of crystallinity as shown in Table 1.

Size-Exclusion Chromatography. Molecular weight averages, molecular weight distributions, and degree of branching were determined by a Viscotek TDA model 301 triple detector array SEC apparatus (viscometer, refractive index detector, and light scattering detector) equipped with two GMHHR-M columns with TSK-gel (mixed bed, MW resolving range 300−100 000, from Tosoh Biosep), a Viscotek VE 5200 GPC autosampler, a Viscotek VE 1121 GPC solvent pump, a Viscotek VE 5710 degasser, and a Viscotek OmniSEC software (version 4.0), all from Viscotek Corp. Tetrahydrofuran stabilized with hindered phenol (250 ppm) was used as mobile phase at the velocity of 1.0 mL/min. Narrow and broad linear polystyrene standards were used for universal calibration, and flow-rate fluctuations were corrected by use of toluene as an internal standard. Columns and detectors were kept at 35 °C.

The branching frequency and the Mark−Houwink α value were both used to characterize the degree of branching in the synthesized polyesters. The number of branches (B_n) was calculated through the Zimm−Stockmayer equation for a polydisperse, randomly branched polymer:[37]

$$g = \frac{6}{B_n}\left[\frac{1}{2}\left(\frac{2+B_n}{B_\text{n}}\right)^{1/2} \ln\left(\frac{(2+B_n)^{1/2}+{B_n}^{1/2}}{(2+B_n)^{1/2}-{B_n}^{1/2}} - 1\right)\right] \quad (1)$$

The entity g is obtained from the intrinsic viscosity of the branched polymer, $[\eta]_\text{Br}$, and the intrinsic viscosity of a linear polymer of the same molecular weight, $[\eta]_\text{L}$, with the shape factor (ϵ) set to 0.75:

$$g = \left(\frac{[\eta]_\text{Br}}{[\eta]_\text{L}}\right)^{1/\epsilon} \quad (2)$$

The branching frequency (λ) is obtained by normalizing the number of branches (B_n) to the molecular weight (M_w) and the repeating unit (R) according to

$$\lambda(M) = \frac{RB_n}{M_\text{w}} \quad (3)$$

The Mark−Houwink α value was obtained from plotting log intrinsic viscosity versus log molecular weight:

$$[\eta] = \text{KM}^{\alpha} \quad (4)$$

The branched polyesters PBA-B1, -B2, and -B3 had significantly lower α-values than the linear polyester PBA-L (see Table 1). This indicates a more spherical molecular structure and significant branching, especially in the case of PBA-B3. Mark−Houwink α values around 0.3−0.4 have earlier been reported for hyperbranched polymers.[38,39]

Differential Scanning Calorimetry. The melting temperatures and the degree of crystallinity were determined on a Mettler-Toledo DSC 820 under nitrogen atmosphere. Dried polymer (5−10 mg) was encapsulated in a 40 μL aluminum cap without pin. Samples were heated from 25 to 120 °C at a rate of 5 °C/min under a nitrogen gas flow of 80 mL/min. The degree of crystallinity, w_c, for the polyesters was calculated as

$$w_\text{c} = \frac{\Delta H_\text{f}}{\Delta H_\text{f}^{\circ}} \quad (5)$$

where ΔH_f is the measured heat of fusion and $\Delta H_\text{f}^{\circ}$ is the theoretical heat of fusion for a 100% crystalline PBA, 135.0 J/g.[40,41] The glass transition of solution cast films was only observed if the samples were quenched, and it was difficult to determine the T_gs of the blends with certainty but all films were soft and pliable at room temperature, indicating a T_g below room temperature. The results indicated a single glass transition for all blends except those containing the hyperbranched polyester PBA-B3. In these blends, two glass transitions were seen.

Hydrolysis. PVC/PBA films (0.2 g) containing 20 and 40 wt % PBA were aged in 50 mL glass vials containing 4 mL of water (HPLC-grade from Fluka, Buchs, Switzerland). The vials were sealed by 5-mil

Teflon white-faced white silicone septa (20 mm diameter and 0.125-in. thick) from Supelco (Bellefonte, PA). All films were aged at 24 °C for 6 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.[42] The ISOLUTE ENV+ column was conditioned with 1 mL of methanol and equilibrated with 1 mL of water (pH < 2). The pK_a values of our expected analytes are 14.7 and 15.5 for 1,4-butanediol and 4.41 and 5.41 for 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 of water) was added to 3 mL of sample solution before it was applied to the SPE column. After the sample was passed through, 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 converted 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 in order 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 (30m × 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 a heating rate of 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 and 250 °C, respectively. The injector temperature was set to 250 °C. Sample (1 μL) was injected in splitless injection mode and five blanks were run between each sample by injection of clean methanol and diethyl ether. 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 comparison of their EI mass spectra to mass spectra included in the reference library NIST 98 (National Institute of Standards and Technology, Gaithersburg, MD), or to previously obtained EI mass spectra that have been confirmed by quasi-molecular ions obtained in chemical ionization mode, CI, with methane as a reagent gas.

Water Absorption and Weight Loss. Water absorption of aged films was measured by weighting the cautiously wiped films before letting them dry in a desiccator until constant weight. After the films were dried to constant weight, weight loss was calculated. Water absorption was calculated from the dry weight:

$$\text{water absorption (\%)} = \left[\frac{\text{wet weight} - \text{dry weight}}{\text{dry weight}}\right] \times 100 \tag{6}$$

Fourier Transform Infrared Spectroscopy. Infrared spectra of synthesized polyesters and solution-cast films were recorded on a Perkin-Elmer Spectrum 2000 FTIR spectrometer (Norwalk, CT) equipped with a single-reflection attenuated total reflectance (ATR) accessory (golden gate) from Graseby Specac (Kent, U.K.). The corrected area was used to calculate the ratio of carbonyl groups to carbon chlorine bonds at the surface and miscibility was assessed by the shifting of the carbonyl group absorption band.

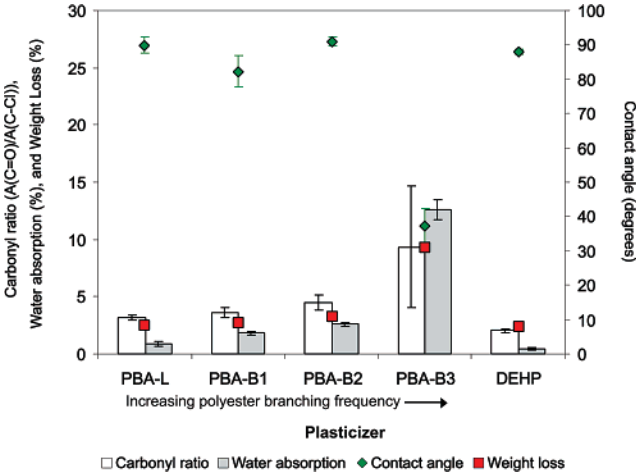

Figure 1. Water absorption, weight loss, contact angle, and carbonyl ratio at the surface of films plasticized with 20 wt % plasticizer.

Static Contact Angle, θ_e. The hydrophilicity of the films' surfaces was also measured by static (equilibrium) contact angle in the sessile drop configuration on a CAM 200 from KSV Instruments Ltd. KSV Instruments CAM 200 software was used to analyze the pictures. A 5 μL drop was placed on the surface by use of the stroke mode and a drop rate of 2 μL/s. A recording speed of 10 pictures/s was used.

Tensile Testing. Tensile testing of solution-cast films before and after aging was conducted in an Instron 5566 equipped with pneumatic grips and Instron series IX software (Bristol, U.K.). Five dry samples of uniform shape (80 × 5 mm) were cut by use of an EP 04/80 × 5 mm 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 with a digital thickness gauge (Mitutoyo micrometer), and elongation at break was calculated from grip separation. ASTM standard D 882-02 was followed with the exception of conditioning procedures. Tensile modulus of elasticity was not measured due to insufficient sample lengths.

Thermogravimetric Analysis. Thermal stability of plasticized films was analyzed on a Mettler-Toledo TGA/ SDTA 851e. Approximately 6 mg of PVC/PBA films containing 20 and 40 wt % PBA was put in a 70 μL alumina cup. Samples were heated from 35 to 600 °C at a rate of 10 °C/min under oxygen gas flow of 50 mL/min.

Results and Discussion

The use of flexible PVC in medical devices is an important part of healthcare all around the world. More strict legislation[3,11,12,43] concerning the use of phthalate plasticizers in childcare articles or medical devices strongly indicates a need for new solutions. One attractive alternative is to replace the reproduction-disturbing traditional plasticizers with nontoxic polymeric plasticizers. Four aliphatic polyesters, poly(butylene adipate) (PBA) with varying degree of branching, were synthesized and solution-cast with PVC as reported in an earlier paper[36] and evaluated for migration resistance, preservation of material properties, and thermal stability.

Migration Resistance. High concentration of polyester at the film surface increases the hydrophilicity of the surface compared to films having a larger amount of PVC at the surface. Higher water absorption is expected for more hydrophilic material since the hydrophilic surface facilitates the migration of water into the material. In the 20 wt % polyester films, an increasing ratio of carbonyl groups to chlorine atoms, that is, a higher concentration of polyester, was detected at the surface as the degree of branching increased (Figure 1). The increasing number

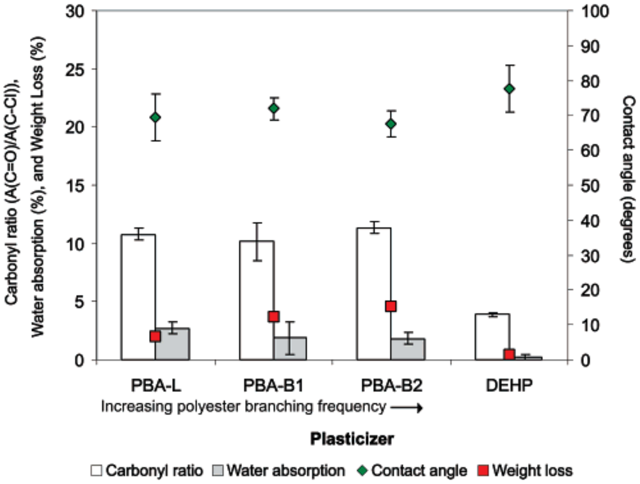

Figure 2. Water absorption, weight loss, contact angle, and carbonyl ratio at the surface of films plasticized with 40 wt % plasticizer.

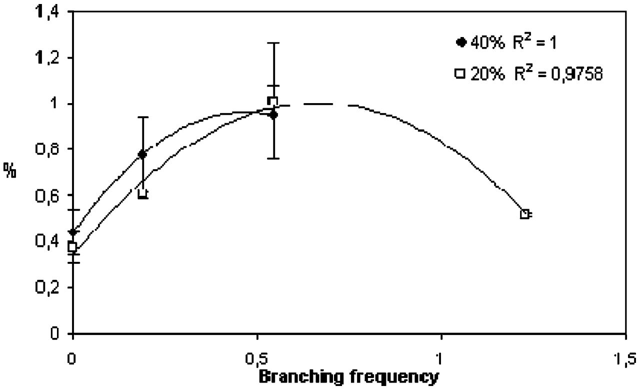

Figure 3. Relative amount of adipic acid released from films plasticized with 20 or 40 wt % polymeric plasticizers during aging in water at 24 °C for 6 weeks plotted vs branching frequency of corresponding polymeric plasticizer. A similar relationship was seen if the relative amount of adipic acid was plotted as a function of polyester polydispersity.

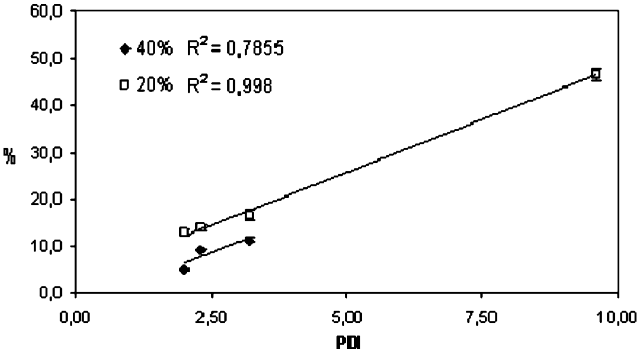

Figure 4. Relative weight loss of films plasticized with 20 or 40 wt % polymeric plasticizers during aging in water at 24 °C for 6 weeks plotted vs polydispersity index of corresponding polymeric plasticizer.

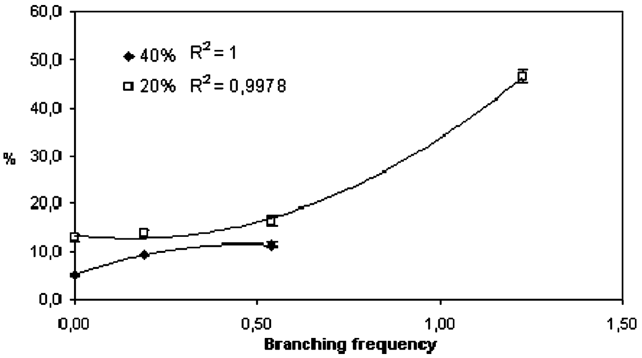

Figure 5. Relative weight loss of films plasticized with 20 or 40 wt % polymeric plasticizers during aging in water at 24 °C for 6 weeks plotted vs branching frequency of corresponding polymeric plasticizer.

Table 2. Low Molecular Weight Oligomers Migrating from Films Plasticized with 20 and 40 wt % Polymeric Plasticizer

plasticizer	AA−BD dimer	AA−BD dimer-ring	AA−BT dimer
PBA-L 20%	X	X	
PBA-L 40%	X	X	
PBA-B1 20%	X	X	
PBA-B1 40%	X	X	
PBA-B2 20%	X	X	
PBA-B2 40%	X	X	X
PBA-B3 20%			X

of chain ends associated with branched or low molecular weight compounds reduces the surface free energy of that compound. Surface enrichment of low molecular weight or branched components in blends with higher molecular weight linear polymers have been shown for other polymer blend systems.[22,44−46] As seen in Figure 1, simultaneously and in good correlation with the increasing carbonyl ratio at the blend surface, water absorption and weight loss increased with increasing degree of branching in the films containing 20 wt % polyester. The contact angle was substantially lower for the blend containing highly branched PBA-B3, which also confirms the higher surface hydrophilicity of the PVC/PBA-B3 blend.

The films plasticized with 40 wt % polyester all absorbed similar amounts of water, irrespective of the structure of the polyester. This is in correlation with very similar carbonyl ratios and surface hydrophilicities for all the films containing 40 wt % polyester (Figure 2). PVC/polyester miscibility is based on intermolecular interactions between the carbonyl group in the polyester and CHCl group in PVC.[14,47−50] Good miscibility and strong intermolecular interactions will enable the polymer chains to pack closer together as miscible polymer pairs undergo densification on mixing.[19] Strong intermolecular interactions reduce the surface segregation and make it more difficult for small molecules to penetrate the material. In an earlier study, better miscibility through intermolecular interactions was seen for the 40 wt % PVC/ PBA blends compared to the 20 wt % blends.[36] This could, thus, explain the similar or lower water absorption of films plasticized with 40 wt % polyester compared to films containing 20 wt % polyester, in spite of the higher hydrophilicity and carbonyl ratio of these films. Consequently, the miscibility and close packing of the polymer chains appears more important for reducing water uptake than the hydrophilicity of the surface.

Migration during Aging. Migrating of low molecular weight compounds from the films during aging in water was followed by measuring the weight loss and by quantification of adipic acid, the monomeric hydrolysis product of PBA. Prior to identification and quantification by GC-MS, the migrated low molecular weight products were isolated from the aqueous medium by solid-phase extraction. Migration as measured by weight loss increased with increasing degree of branching for both 20 and 40 wt % blends, and the release of adipic acid during aging was higher for films containing a higher concentration of plasticizer.

The relative amount of adipic acid released in relation to the amount of polyester originally present in the films was approximately the same for films containing 20 and 40 wt %

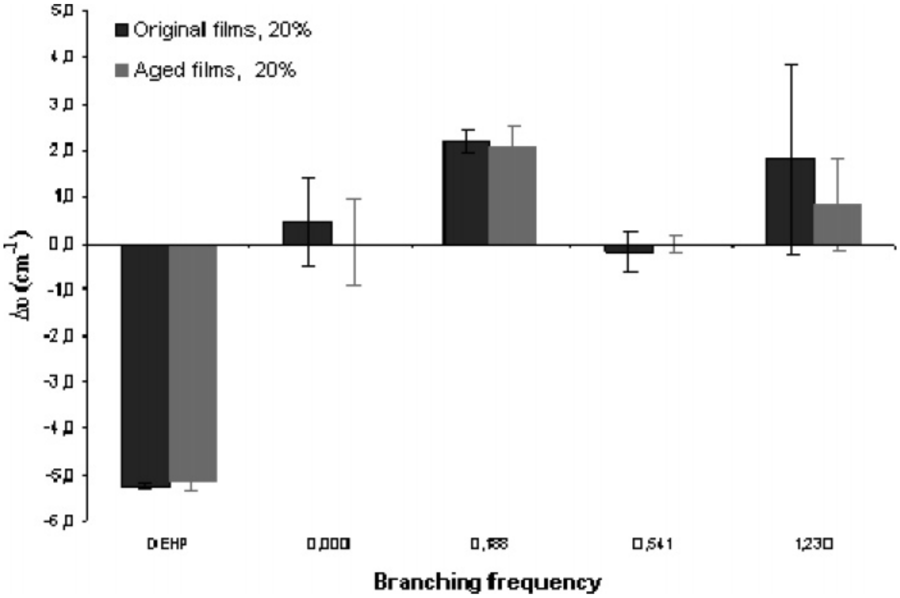

Figure 6. $\Delta\upsilon$ vs branching frequency for PVC films plasticized with polyesters and phthalate plasticizers at 20 wt % concentration.

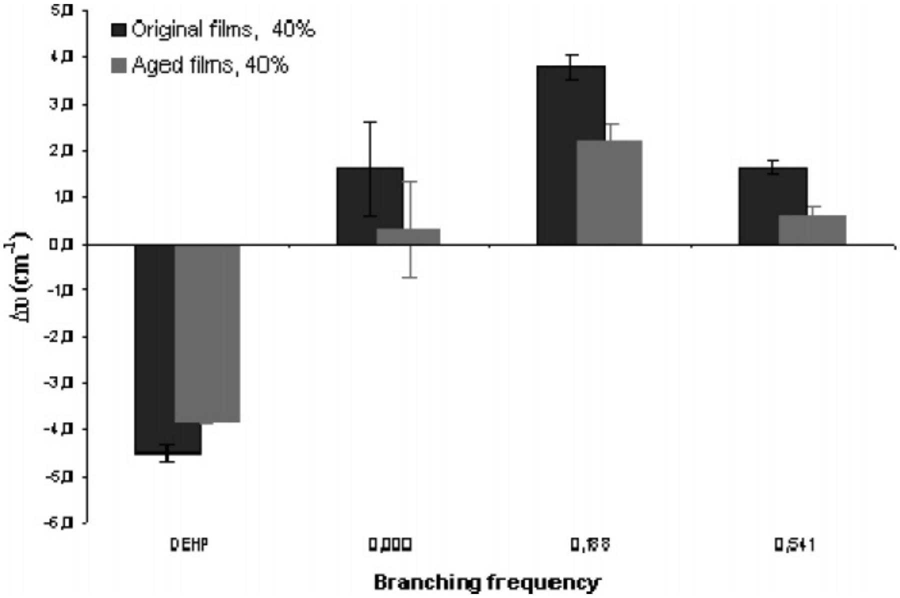

Figure 7. $\Delta\upsilon$ vs branching frequency for PVC films plasticized with polyesters and phthalate plasticizers at 40 wt % concentration.

plasticizer (Figure 3). It is possible that the small amount of adipic acid detected is present in films from the beginning and correlates to the increasing polydispersity and higher branching frequency of the more branched polyesters. The reason for the lower amount of adipic acid migrating from films plasticized with the highly branched PBA-B3 compared to the other films is probably the low amount of DMA left unreacted in the highly branched PBA-B3 polyester due to the higher ratio of hydroxyl groups to methyl ester groups during synthesis of PBA-B3 combined with the low amount of methyl ester end groups. The weight loss for films plasticized with the highly branched PBA-B3 polyester was, however, large, which indicates that the material had poor migration resistance.

The relative weight loss, that is, weight percent of the original polyester that had migrated from the film, was considerably larger for films containing 20 wt % of polyester compared to those containing 40 wt % polyester (Figures 4 and 5). The weight loss increased with increasing polydispersity and with increasing degree of branching for both 20 and 40 wt % blends. The relative weight loss was in almost linear relation to the polydispersity index of the polyester plasticizers, especially at the 20 wt % concentration (Figure 4). This correlation highlights the importance of reducing the amount of low molecular species present in the film in order to increase the migration resistance. The difference between relative weight loss and relative amount of adipic acid shows that a larger amount of oligomers migrated from the films containing 20 wt % polyester compared to the films containing 40 wt % polyester. Lower amount of intermolecular interactions and a less densely packed matrix facilitates molecular transfer[36] and could explain the larger weight loss seen in films containing 20 wt % compared to those containing 40 wt % polyester. The more closely packed chains in the blends with 40 wt % plasticizer probably both reduce water absorption and prevent oligomeric species from migrating from the material. Strong intermolecular interactions between the chains also decrease the mobility of oligomeric species,[51] which reduces the migration rate.[20,52,53]

Oligomers. Low molecular weight oligomers migrating from the films with 20 and 40 wt % polyester plasticizer were also identified by GC-MS. Three different dimers, identified as adipic

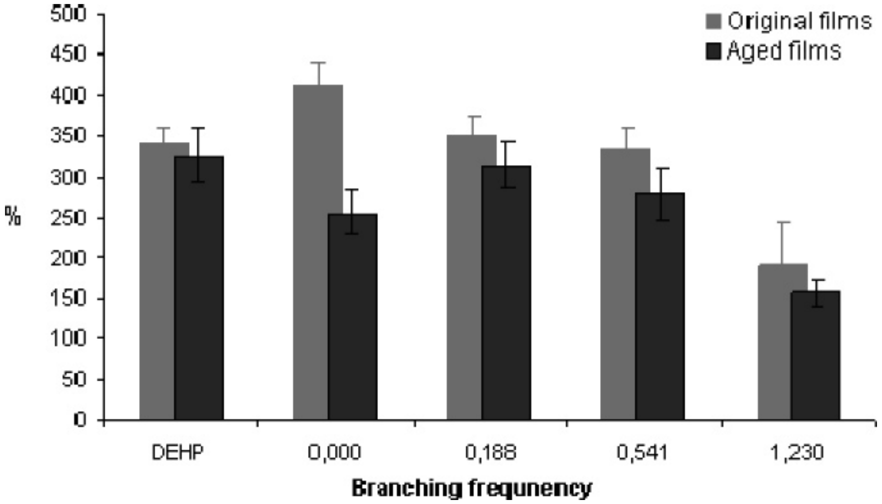

Figure 8. Strain at break vs branching frequency for PVC films plasticized with polyesters and phthalate plasticizers at 20 wt % concentration.

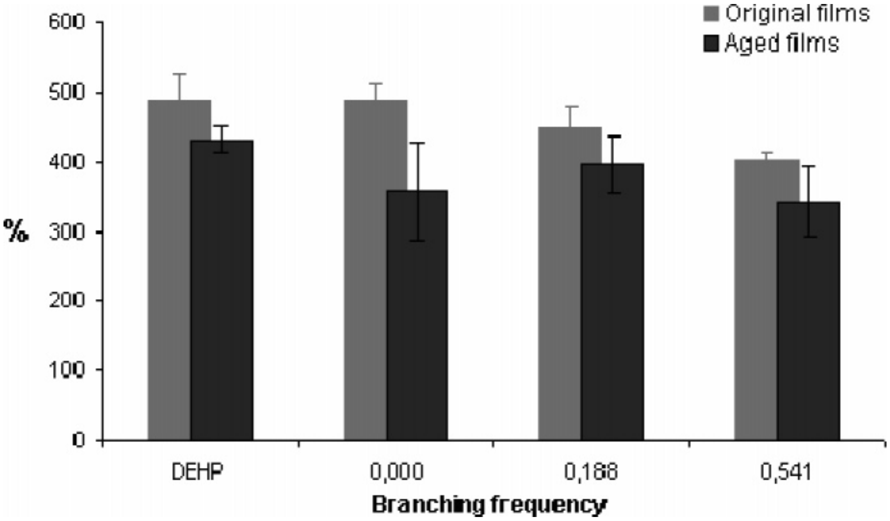

Figure 9. Strain at break vs branching frequency for PVC films plasticized with polyesters and phthalate plasticizers at 40 wt % concentration.

acid−1,4-butanediol dimer (AA−BD), possibly adipic acid−1,4-butanediol ring-formed dimer (AA−BD-ring), and most likely adipic acid−1,2,4-butanetriol dimer (AA−BT), were detected migrating from films according to Table 2.

Preservation of Material Properties. When polymeric materials are used in applications like medical devices or toys, the contact with biological fluids induces material degradation either by a direct attack on the polymer chains or by accelerating the leaching of low molecular weight additives. The loss of plasticizer causes changes in both physical and mechanical properties of the material and affects the possibilities for continued use of the device.

Miscibility. Shifting of the carbonyl group absorption band in PVC/polyester blends is an indication of miscibility through intermolecular interactions.[14,47−49] There was a considerable standard deviation in the shifting of the carbonyl absorption band for the films plasticized with 20 wt % plasticizer, which indicates large and unfavorable heterogeneity in these blends. The only exceptions were the blends containing the slightly branched PBA-B1 and the traditional plasticizer DEHP, which both had a significant shift (Figure 6). In the films containing 40 wt % plasticizer (Figure 7), significant shifting of the carbonyl absorption band was seen for all blends before aging. After aging, however, especially the films containing slightly branched polyester PBA-B1 but also the films containing branched PBA-B2 still showed a significant shift, but the films containing linear polyester PBA-L did not. This shows that slight branching in the polyester plasticizer improves the preservation of material properties during aging. These results are in good agreement with our earlier results,[34] where a slightly branched polyester (Mark−Houwink α value = 0.543) showed superior miscibility over linear polyesters in solution-cast PVC/PBA films. The presence of significant shifting in films containing 40 wt % polyester but not in most of the films containing 20 wt % polyester also confirms the presence of stronger intermolecular interactions at this composition and is in good correlation with low water absorption and weight loss.

Aging of solution-cast PVC/PBA films in water for 6 weeks induced migration of both monomeric and oligomeric species to the aging medium. The ratio of carbonyl groups to chlorine atoms at the surface of the films generally increased as a result of aging, as did the crystallinity, indicating migration of polyester to the surface and formation of polyester crystals. The exception to this was the highly branched PBA-B3, which decreased in crystallinity as a result of aging. Surface enrichment of crystalline poly(caprolactone) (PCL) compared to the amorphously blended bulk was also seen by Clark et al.[21] for the PVC/PCL system.

Mechanical Properties. Mechanical properties of original films and films aged in water for 6 weeks were evaluated by tensile testing. Before aging, films with the linear polyester PBA-L showed the longest elongation at break. However, this

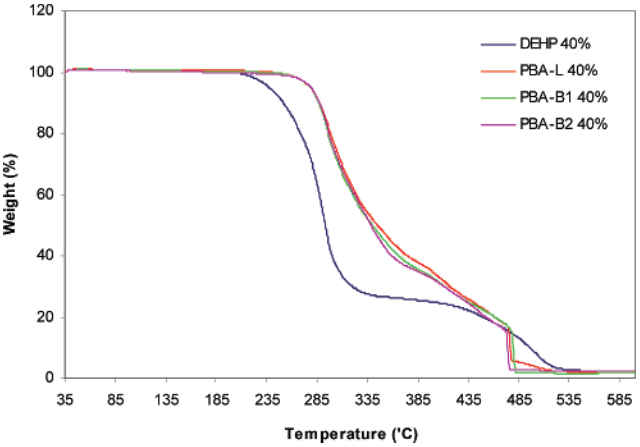

Figure 10. TGA curve showing the sample weight as a function of temperature for films plasticized with 40 wt % plasticizer.

film did not maintain its mechanical properties well during aging, and films plasticized with the slightly branched polyester PBA-B1 proved most ductile of the polymeric plasticizers. In correlation with the shifting of the carbonyl group absorption band, this indicates that a slightly branched polymeric plasticizer supports the preservation of good mechanical properties during aging (Figures 8 and 9). This is in good agreement with our earlier results,[34] where blends of PVC and a slightly branched polyester (Mark−Houwink α value = 0.543) showed larger tensile elongation than PVC films plasticized with a linear polymeric plasticizer. The tensile stress was generally similar among PVC/polyester blends and it was reduced as a consequence of aging. Films plasticized with the highly branched polyester PBA-B3, however, experienced increased stress as a result of aging.

Thermal Stability. PVC is a heat-sensitive material and it needs heat stabilizers to withstand the temperatures used during processing. Traditional heat stabilizers contain heavy metals and have been substituted by alternative stabilizers when possible. Apart from having a plasticizing effect on PVC, the addition of polymeric plasticizers can also improve the high-temperature stability of the material.[54,55] In order to slow down the catalytic effect of hydrogen chloride (HCl),[55,56] polyesters react with the HCl that is split off from the PVC chain. In the process, carboxylic acids or acid chlorides are formed that have a weaker catalytic effect on the continued dehydrochlorination of PVC than HCl.[54,55] Films plasticized with 20 and 40 wt % polymeric plasticizers, PBA-L to PBA-B3, were therefore analyzed with respect to thermal stability, and the results were compared to thermal stability of films plasticized with the traditional plasticizer DEHP. Films with 40 wt % polymeric plasticizer had higher onset temperatures of degradation and improved heat stability compared to films with a traditional plasticizer as can be seen in Figure 10. For films containing 20 wt % plasticizer, the initial weight loss was larger for films containing the polymeric plasticizers than for films plasticized with DEHP, but as the temperature increased, films with traditional plasticizer were degraded faster. The heat-stabilizing effect of PBA-L, PBA-B1, and PBA-B2 was the same, but the films plasticized with PBA-B3 were less thermally stable than films plasticized with traditional plasticizer DEHP or the other polymeric plasticizers.

Conclusions

Improved migration resistance, long-term properties, and thermal stability in PVC/polyester blends were obtained by proper design of plasticizer architecture. Strong intermolecular interactions probably lead to tighter packing of the polymer chains, which reduced water absorption and migration of oligomers from the blends even when the hydrophilicity of the blends increased. PVC blended with slightly branched polyester was the material that best preserved material and mechanical properties during aging. Increasing degree of branching for the polyester was accompanied by increased hydrophilicity and polydispersity, as well as reduced miscibility and migration resistance in the blends. Polyester plasticizers with no, low, or moderate degrees of branching improved the thermal stability of the films compared to films plasticized with a traditional phthalate plasticizer, and the effect increased with increasing plasticizer concentration.

Acknowledgment. Professor Ann-Christine Albertsson is thanked for valuable discussions during this work.

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BM070001K