Environmentally Friendly Plasticizers for Poly(vinyl chloride)—Improved Mechanical Properties and Compatibility by Using Branched Poly(butylene adipate) as a Polymeric Plasticizer

Annika Lindström, Minna Hakkarainen

Department of Fiber and Polymer Technology, Royal Institute of Technology, Stockholm, Sweden

ABSTRACT: Linear and branched poly(butylene adipate)s (PBA) with molecular weights ranging from 2000 to 10,000 g/mol, and a branching agent content between 0 and 1.8%, were solution cast with poly(vinyl chloride) (PVC) to form 50- to 60-μm thick flexible films. Dry films were analyzed by tensile testing, Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), and optical microscopy (OM) to study the effects of molecular weight and branching on the plasticizing efficiency of the polyester. PBA formed a semimiscible two-phase system with PVC, where the amorphous part exhibited a single glass transition temperature. The degree of crystallinity for the polyester, surface composition, and mechanical properties of the films depended on the blend composition, molecular weight, and degree of branching of the polyester. Plasticizing efficiency was improved by higher degree of branching. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 2180–2188, 2006

Key words: poly(vinyl chloride); poly(butylene adipate); plasticizer; blends; mechanical properties

INTRODUCTION

Poly(vinyl chloride) (PVC) is today one of the most important plastic materials available in terms of consumption. It has a broad collection of applications in different areas, and flexible PVC grades are obtained by compounding PVC with plasticizers. The most significant group of PVC plasticizers is phthalate esters. They constitute 97% of the total amount of plasticizers used and are usually added in concentrations up to 50% of the final weight of the products. Phthalate esters are low molecular weight compounds that are easily released from the polymer matrix. They have been found in most environments, in domestic foods and wastes, in animals and humans.[1] When used in applications such as medical devices or toys, the contact with biological fluids or synthetic substitutes accelerates the migration of low molecular weight additives, causing changes in the long-term properties of the material and possible toxic and biological effects arising from the transfer of plasticizer to humans.[1–6]

In December 1999, the European Commission issued an emergency ban (1999/815/EG) on the use of six phthalate esters (diisononyl phthalate, diisodecyl phthalate, bis(2-ethylhexyl) phthalate (DEHP or DOP), dibutyl phthalate, benzyl butyl phthalate, and di-*n*-octyl phthalate) in toys and childcare articles that are intended to be placed in the mouth of children under the age of three.[7] This ban was renewed in August 2003[1] but some EU members already apply more stringent restrictions where products that are likely, or can be placed in the mouth of children under the age of three are concerned as well. Following the European ban, also other countries including USA and Canada have introduced regulations regarding the use of these phthalate esters in toys intended for mouthing.[1]

Both alternative plasticizers and substitute plastic materials have been assessed for the replacement of phthalate-plasticized PVC. The key issues for a successful substitution of phthalate-plasticized PVC is to find a material possible to process in conventional processing equipments, a material that forms products matching the technical requirements, and a material that can be manufactured at a comparable cost. Phthalate plasticizers provide a broad range of properties when compared with those of many other plasticizers such as phosphates, epoxides, aliphatic dibasic esters, trimellitates, pyromellitates, and polymeric plasticizers.[8] The literature reports of PVC blends with different rubber-like materials, e.g., acrylonitrile-butadiene rubber or vinylchloride-ethylene-vinylacetate,[9] and with aliphatic polyesters, including polycaprolactone (PCL),[10–12] poly(3-hydroxybutyrate-*co*-3-hydroxyval-

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

erate),[13] poly(butylene adipate) (PBA),[12,14–16] poly(caprolactone-carbonate) (PCL-PC), and poly(caprolactone-ethylene glycol-carbonate).[17] Among the substitute plastics evaluated, ethylene-vinyl acetate (EVA) copolymers, polyesters, blow-molded polyolefins and laminates have been found to offer additional property benefits to some applications,[2,18] though often at the expense of original application performance. However, in many applications no material has yet been found that can satisfactorily substitute soft PVC, and no low molar mass plasticizer has so far been capable of replacing phthalate esters without inducing migration. Coatings based on poly(ethylene oxide)[19] or surface modification by radiation crosslinking[20] often reduce migration at the cost of other properties. 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.

A low molecular weight plasticizer is easily mixed with the polymer resin and its high density of chain-ends induces much free volume in the material. At a given phr ratio, a plasticizer with a higher hydrodynamic volume, i.e. a more bulky plasticizer, reduces the strength, stiffness, and toughness of the material more efficiently than a plasticizer that easily can be packed among the polymer chains.[21] Higher molecular weight of the plasticizer allows more entanglements and provides fewer chain-ends per mass plasticizer. Plasticized with a polymeric plasticizer the material usually becomes more difficult to process than if plasticized with a low molecular weight plasticizer, the tensile strength increases and elongation is reduced.[16] Branched polymers have a higher density of chain-ends compared with that of linear polymers of the same molecular weight, and therefore also more free volume and mobility at the same molecular weight. Using a branched polymeric plasticizer would thus increase the mobility of the system when compared with a system plasticized with a linear polymer at the same time as the branched polymer's high molecular weight and bulkiness significantly reduce its volatility and diffusivity compared with low molecular weight plasticizers.

PVC and aliphatic polyesters are miscible probably through hydrogen bonding between the carbonyl group of the ester and the α-hydrogen next to the chlorine atom in PVC. The intermolecular force might also originate from hydrogen bonding between the carbonyl group of the ester and a β-hydrogen in PVC, or from a dipole–dipole interaction between the carbonyl group of the ester and the chlorine atom in PVC.[12,22–25] The miscibility of polyester/PVC blends have been shown to be favored by a polyester CH_2/$C=O$ ratio of 4–10,[12,14] and flexible films of PVC and polyesters have been found miscible in the amorphous state in all compositions.[10,17,22] Recently Choi and

TABLE I
Amounts 1,4-butanediol, Adipic Acid, Dimethyl Ester of Adipic Acid, Trimethylol Propane, and Titanium Isopropoxide Added to Synthesize Different PBA Polyesters

Polyester	BD:Acid[a,b]	Acid[a]	TIP (mole %)	TMP (mole %)
PBA-L1	1.05:1.0	AA	0.15	—
PBA-L2	1.0:1.0	AA	0.2	—
PBA-L3	1.06:1.0	DMA	0.1	—
PBA-B1	1.05:1.0	AA	0.1	0.5
PBA-B2	1.0:1.0	DMA	0.2	1.5
PBA-B3	1.0:1.0	AA	0.2	0.26
PBA-B4	1.0:1.0	DMA	0.2	3.0

BD, 1,4-butanediol; TMP, trimethyl propane; TIP, titanium isopropoxide.
[a] Generic term for adipic acid (AA) and dimethyl ester of adipic acid (DMA).
[b] Molar ratio (mole:mole).

Kwak reported on the use of hyperbranched poly(ε-caprolactone)[26] and another highly branched, patented polyester[27] 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.[26,27] We have in earlier studies investigated PVC/poly(caprolactone-carbonate) blends[28] and as far as we know there are no earlier studies on how low degree of branching affects the properties of PVC/polyester blends, and the aim of this work was to evaluate how macromolecular structure affects the polyester plasticizer efficiency and blend properties.

EXPERIMENTAL

Synthesis of the polyesters

1,4-butanediol (BD) (99%), adipic acid (AA) (99%), dimethyl ester of AA (DMA) (~99%), dimethyl ester of succinic acid (DMS) (98%), and trimethylol propane (TMP) (>98%) as branching agent were purchased from Fluka and used as received. Titanium isopropoxide (TIP) (99.99%) was used as a catalyst for the reaction, chloroform and diethyl ether were obtained from Sigma-Aldrich. Methanol was obtained from Merck Eurolab. To synthesize linear PBA (PBA-L1, -L2, -L3), BD and DMA or AA were weighted and added to a two neck round-bottom reaction vessel in the amounts reported in Table I. TIP catalyst was added to each reaction mixture. The reaction vessel was immersed in a silicon oil bath and the temperature was increased under nitrogen gas to 130°C where the reaction was continued for 3 h. The methanol formed in the reaction was continuously distilled from the reaction mixture. The temperature of the reaction mixture was then raised to 180°C under reduced pressure and the polymerization was continued for 16 h.

After the polymerization was completed the reaction mixture was cooled down to room temperature. The polyesters were dissolved in chloroform and removed from the reaction vessel. The polymers were precipitated into methanol, filtrated, and washed with diethyl ether. Branched PBA polymers (PBA-B1, -B2, -B3, -B4) were synthesized in a similar way by adding BD, DMA or AA, and TIP catalyst in the amounts reported in Table I to a two-neck round-bottom reaction vessel. PBA-B1 was first kept 1 h at 140°C, where after the temperature was raised to 200°C for 1 h and 40 min. The reaction mixture was cooled to room temperature and 0.5 mol % TMP was added. The reaction was continued for 6 h at 180°C under reduced pressure before the temperature was raised to 200°C and the polymerization was continued for 16 h. PBA-B2 was in the first step reacted 2 h at 130°C. The reaction was continued for 3 h at 130°C after the addition 1.5 mol % TMP. The temperature was then raised to 180°C under reduced pressure and the polymerization was continued for 16 h. PBA-B3 was reacted 2 h at 130°C after which the temperature was raised to 160°C under reduced pressure for 16 h. 0.26 mol % TMP was added to the reaction mixture and the polymerization was continued for first 3.5 h at 130°C and then 3.5 h at 180°C under reduced pressure. The last polyester, PBA-B4, was reacted 2 h at 130°C before 3.0 mol % TMP was added. The reaction was then continued at 130°C for 2 h. The polymerization was finalized at 180°C under reduced pressure for 24 h.

Size exclusion chromatography

Molecular weight of synthesized polyesters was determined using a Viscotek TDA model 301 triple detector array SEC apparatus (viscometer, refractive index detector, and light scattering detector) equipped with GM HHR-M × 2 columns with TSK-gel (Tosoh Biosep), a Viscotek VE 5200 GPC Autosampler, a Viscotek VE 1121 GPC Solvent pump, a Viscotek VE 5710 Degasser, and a Viscotek Trisec 2000 software (Version 1.0.2), all from Viscotek Corp. Tetrahydrofuran stabilized with hindered phenol (250 ppm) was used as mobile phase at the velocity of 1.0 mL/min. Linear polystyrene standards were used for SEC calibration, 11 narrow standards (Mp: 0.580–185 kg/mol) and one broad standard (M_w = 250 kg/mol, PDI = 2.5). Flow-rate fluctuations were corrected using the DRI signal of the injected THF as an internal standard. The right angle laser light scattering detector (RALLS) was calibrated with linear polystyrene standards (M_w = 90.1 kg/mol, PDI = 1.04; M_w = 250 kg/mol, PDI = 2.5; both in concentration, 1.00 mg/mL). Columns and detectors were kept at 35°C.

Nuclear magnetic resonance

1H NMR analyses were conducted on a Bruker Avance 400 Fourier transform nuclear magnetic resonance spectrometer (FT-NMR) operating at 400 MHz. The temperature was 25°C and chloroform-d1 (CDCl3) was used as solvent. Samples were prepared by dissolving 25 mg of polymer in 0.5 mL CDCl3 in 5-mm diameter sample tubes.

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 accessory (golden gate) from Graseby Specac (Kent, UK).

Solution casting

Solution cast PVC/PBA films were prepared by dissolving 2 g (total amount of polymers) in 80 mL of THF (from BergmanLabora, Sweden). Three different ratios of PVC/PBA were prepared for each polyester, i.e., 20, 40, and 60 wt % PBA. The dilute polymer solutions were prepared at 40°C and constant agitation, exception for solutions of PVC/PBA-L1 and PVC/PBA-B2 that were dissolved at 45 and 50°C, respectively. To eliminate possible dust in the synthesized PBAs, the weight portions of polyesters were first dissolved and filtered through a preweighted filter before PVC was added to the solution. The filters were dried until constant weight to ensure no major loss of polyester during this step of the preparation. When both polyester and PVC was fully dissolved, the dilute solutions were cast in clean petri dishes (with lids) that had previously been flushed with compressed air to minimize the presence of dust particles. The films were dried in ambient pressure and room temperature for 3 days and in a vacuum desiccator for additionally 3 days. Dry films were ~50–60-μm thick and kept between light protecting aluminum foils in a desiccator until analysis.

Tensile testing

Tensile testing of solution cast films was conducted in an Instron 5566 equipped with pneumatic grips and Instron series IX software (Bristol, United Kingdom). Five dry samples of uniform shape (80 × 5 mm^2) were cut using a EP 04/80 × 5 mm^2 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

TABLE II
Average Molecular Weights, Polydispersity Index, and Percent Branching Agent in Synthesized PBA Polyesters, Characterized by SEC and NMR

Polyester	M_n (g/mol)[a]	M_w (g/mol)[a]	PDI[a]	TMP (%)[b]	MH a-value[c]
PBA-L1	2,800	3,300	1.4	—	0.582
PBA-L2	4,100	6,100	1.5	—	0.604
PBA-L3	7,800	14,100	1.9	—	0.608
PBA-B1	4,200	6,900	1.6	0.8	0.550
PBA-B2	5,000	8,000	1.6	1.8	0.543
PBA-B3	5,400	8,800	1.6	0.4	0.597
PBA-B4	9,700	17,500	1.8	0.2	0.629

[a] Measured by SEC, universal calibration.
[b] Measured by NMR.
[c] Mark Houwink a-values, measured by SEC, universal calibration.

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 because of insufficient sample lengths.

Differential scanning calorimetry

DSC analyses were performed on a Mettler-Toledo DSC 820 under nitrogen atmosphere. 5–10 mg of dried polymer or polymer film was encapsulated in a 40-μL 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. There after the samples were cooled from 80 to 25°C at a rate of 5°C/min, from 25 to −50°C at a rate of 1°C/min, and from −50 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 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.

Optical microscopy

Polarized light optical microscopy (OM) of solution cast films was conducted using a Leitz Ortholux POL-BK II OM equipped with a Leica DC 300 camera and Leica IM50 software (Version 1.20, Release 19), which was used to process the images.

RESULTS AND DISCUSSION

One way of avoiding the negative effects caused by the migration of plasticizers, and at the same time retaining the good qualities of plasticized PVC, is to substitute low molecular plasticizers with compatible and nontoxic polymeric plasticizers. In this work, linear and branched PBA were synthesized and used as PVC plasticizers in concentrations of 20, 40, and 60 wt % PBA. The synthesized polyesters were characterized by SEC, NMR, and FTIR. The results from SEC and NMR measurements can be seen in Table II. Good correlation was found between Mark Houwink a-values obtained in SEC and the TMP content calculated from NMR spectras, i.e., lower a-values for PBA-B2 and PBA-B1 than those for the other polyesters.

Mechanical properties of PVC/PBA films

Investigation of the mechanical properties of flexible PVC films is a useful first step in evaluating a new plasticizer. Solution cast PVC films plasticized with different amounts of traditional or polymeric plasticizers were therefore analyzed by tensile testing to detect patterns correlating plasticizer efficiency and plasticizer characteristics. The polymeric plasticizers used in this study had different molecular weights and degrees of branching as reported in Table II. Plasticizer concentration proved to be the most important parameter for the plasticizing effects on PVC films for both polyester plasticizers and traditional phthalate plasticizers. As can be seen in Table III, films with 40 wt % plasticizer content showed elastomeric stress–strain curves for all the studied plasticizers while only PBA-B2 and DEHP showed elastomeric stress–strain curves for other concentrations as well, i.e., 20 and 60% respectively. The polymeric plasticizers in general produced a stronger material with rather similar ductility as films containing the traditional low molecular weight plasticizers, see Figures 1 and 2. Within the collection of polymeric plasticizers studied it was however difficult to deduce any specific pattern correlated to the molecular weight of the polyester but a trend of somewhat larger elongation was observed for films plasticized with polyesters having a higher degree of branching (Fig. 1). Higher plasticizing efficiency of branched polyesters is concurrent with a lower packing density of the polymer chains. A higher degree of branching generates more mobile chain-ends and hence increases the free volume in the material.[29] Recent results reported on the mixing of PVC

TABLE III
Tensile Testing Results of PVC/PBA Blends

Plasticizer	Plasticizer conc, (wt %)	Stress at break (MPa)	Strain at break (%)	Stress at upper yield (MPa)	Strain at upper yield (%)
PBA-L1	20	33.5 ± 5.0	321 ± 39	43.5 ± 0.9	7 ± 0.2
	40	**24.6 ± 1.2**	**507 ± 44**	—	—
	60	13.0 ± 2.9	333 ± 87	**14.1 ± 0.8**	**15 ± 0.6**
PBA-L2	20	25.5 ± 6.3	35 ± 27	51.9 ± 4.4	6 ± 0.4
	40	**23.6 ± 1.7**	**523 ± 26**	—	—
	60	10.3 ± 2.2	170 ± 56	**13.0 ± 0.4**	**21 ± 5**
PBA-L3	20	27.4 ± 3.6	187 ± 70	41.2 ± 4.0	7 ± 0.1
	40	23.2 ± 1.8	**504 ± 71**	—	—
	60	14.7 ± 4.3	474 ± 117	**13.6 ± 0.7**	**22 ± 3.4**
PBA-B1	20	33.2 ± 3.4	314 ± 74	24.2 ± 6.3	7 ± 0.5
	40	**23.7 ± 2.1**	**560 ± 77**	—	—
	60	14.7 ± 2.3	388 ± 137	**13.9 ± 0.8**	**26 ± 2**
PBA-B2	**20**	**34.6 ± 1.3**	497 ± 52	—	—
	40	**29.4 ± 1.7**	**617 ± 50**	—	—
	60	10.8 ± 0.7	175 ± 27	**10.4 ± 0.7**	**24 ± 3**
PBA-B3	20	27.5 ± 6.0	187 ± 85	45.7 ± 2.1	7 ± 0.1
	40	**21.1 ± 2.4**	**508 ± 53**	—	—
	60	11.4 ± 3.0	286 ± 102	**12.0 ± 10**	**23 ± 2**
PBA-B4	20	27.8 ± 3.4	284 ± 49	31.9 ± 1.5	7 ± 0.2
	40	**25.6 ± 3.4**	**538 ± 43**	—	—
	60	15.5 ± 2.9	386 ± 142	**15.2 ± 1.3**	**23 ± 2.7**
DOP	20	31.9 ± 2.5	371 ± 41	15.6 ± 0.6	8 ± 0.2
	40	**17.0 ± 2.3**	**562 ± 56**	—	—
	60	6.9 ± 1.0	651 ± 74	**3.9 ± 1.6**	**284 ± 168**
DEHP	20	36.0 ± 2.0	346 ± 46	24.2 ± 1.1	6 ± 0.3
	40	17.6 ± 1.1	533 ± 52	—	—
	60	7.2 ± 0.7	669 ± 70	—	—

Films showing an elastomeric stress-strain curve (i.e. no yield point) in tensile tests are marked as bold.

and hyperbranched PCL with different degree of branching and length of linear segments[26] are in good agreement with our results.

Surface character and miscibility of PVC/PBA films measured by FTIR

A blend of two or more polymers can be defined as totally miscible (microscopically homogenous), partially miscible (microscopically heterogeneous), or immiscible (macroscopically heterogeneous),[30] depend-

ing on the level of homogeneity. One good method for determining miscibility on a molecular level is Fourier transform infrared spectroscopy (FTIR). FTIR was in this study used to analyze the surface composition of plasticized films to see if the two polymers mixed well, or if one of the two polymers was more prominent at the surface. A certain degree of surface enrichment of the component with the lowest surface free energy might occur also in totally miscible blends,[30] but the better the miscibility, the less surface segregation. At 40 wt % polyester, only films plasticized with
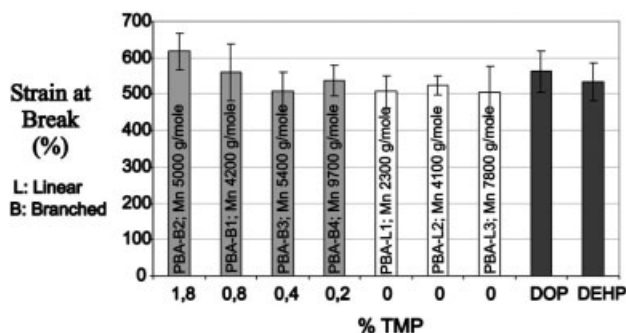

Figure 1 Strain at break *vs.* branching agent content of PVC films containing 40 wt % plasticizer. L, linear polyester plasticizer; B, branched polyester plasticizer.
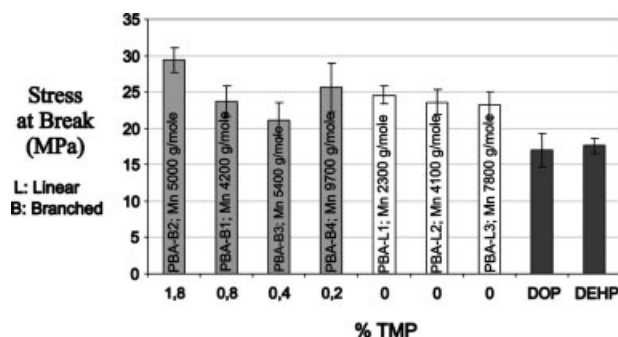

Figure 2 Stress at break *vs.* branching agent content of PVC films containing 40 wt % plasticizer. L, linear polyester plasticizer; B, branched polyester plasticizer.

TABLE IV
Surface Character of Plasticized Films Analyzed by FTIR

	20% PC			40% PC			60% PC		
	A	B	C	A	B	C	A	B	C
PBA-L1	•					•			•
PBA-L2		•				•			•
PBA-L3	•					•			•
PBA-B1	•					•			•
PBA-B2	•				•				•
PBA-B3		•				•			•
PBA-B4	•				•				•
DOP	•			•			•		
DEHP	•			•			•		

PC, plasticizer concentration. Film surface character: A, FTIR spectra of films contained absorption peaks characteristic for both PVC and the plasticizer used; B, FTIR spectra of films were more similar to the spectra of pure PVC than to that of pure plasticizer; C, FTIR spectra of films were more similar to the spectra of pure plasticizer than to that of pure PVC.

PBA-B2 and PBA-B4 displayed FTIR spectra containing an evident mixture of the pure PVC spectra and the original polyester spectra, see Table IV. In correlation, blends containing PBA-B2 and PBA-B4 also proved strongest in the tensile testing mentioned in the previous section, Figure 2. The other films containing 40 wt % plasticizer all exhibited spectra more similar to the original polyester than that to pure PVC, indicating a domination of plasticizer at the surface. These results are concurrent with results found by Clark et al.[30] for the PVC/PCL system where a surface enrichment of crystalline PCL was observed when compared with the amorphously blended bulk. Blends containing 20 wt % PBA-B2, i.e., the only PVC/PBA films showing elastomeric stress–strain curves at 20 wt % plasticizer, also displayed a clearly mixed surface spectra, which can be seen in Figure 3. Films plasticized with traditional phthalate plasticizers showed spectra indicating a clearly mixed surface compositions at all concentrations.

Miscibility of PVC and esters/polyesters has in multiple studies been analyzed by observing a shift of the carbonyl group stretch absorption band by FTIR. Such a shift toward lower frequencies compared with the absorption band frequency of the carbonyl group in the pure plasticizer was observed for films plasticized with traditional plasticizer. This result for the phthalate plasticizers is in good agreement with several studies on the shift of the carbonyl group absorption band in the molten or amorphous state because of interactions between the carbonyl group in PCL, and a α-hydrogen in PVC (hydrogen bonding), or between the carbonyl group and the chlorine atom (dipole–dipole interaction).[12,22–25] However, for films plasticized with polymeric plasticizers a shift toward higher frequencies compared with the absorption band fre-

quency of the carbonyl group in the pure plasticizer was observed. In a PVC/polyester system it is usual that the polyester crystallizes and that the system therefore consists of a two-phase system with one part of crystalline polyester and one part of amorphous miscible PVC/polyester. Many studies have been done on the two-phase miscible PVC/PCL system.[11,30–32] The carbonyl group stretch absorption band from the ester groups in PCL consists of one part due to the crystalline domains and one part due to the amorphous domains. The crystalline domains give rise to an absorption band at lower frequencies than that of the amorphous domains. When specific interactions between PVC and PCL are favorable, the amorphous part of the band is more intense, and as a result of the specific interactions, the amorphous part of the absorption band is shifted toward lower frequencies while the crystalline part is shifts toward higher frequencies.[11] By comparing experimental spectra of PVC/PCL blends with simulated spectra, Canavate et al.[31] confirmed the results of Coleman and Zarian[11], showing that because of the interactions between PVC/PCL, a new band is formed between the amorphous and crystalline band. A shift of the carbonyl group absorption band toward higher frequencies in amorphous PVC/PCL systems compared with pure semicrystalline PCL have also been reported from Karal et al. in 1997[33] and Penco et al. in 2002.[32] The shift of the carbonyl group stretch absorption band observed for polyester plasticized films in this study can thus be confirmed as an indication of the presence of specific interactions between the PVC and PBA. The shift toward higher frequencies also concurs well with the significantly lower degree of crystallinity of PBA in the blends as reported in later sections below. As can be seen in Table V, generally slightly larger shifts were measured for films with 20 wt % PBA than that for films with higher plasticizer content.
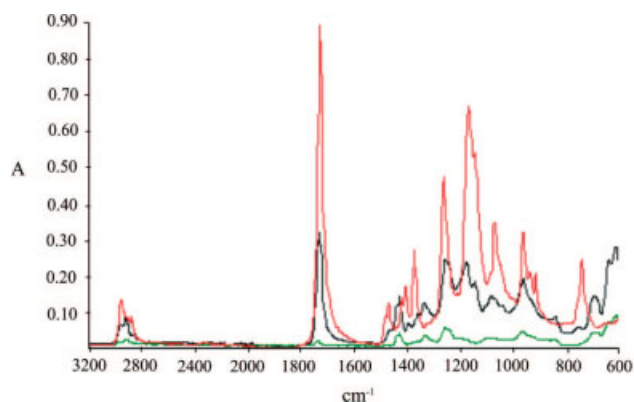

Figure 3 FTIR surface spectra of PVC plasticized with 20 wt % PBA-B2. The lower line is the spectra of pure PVC, the line in the middle is the surface spectra of PVC/PBA-B2, and the upper line is the spectra of pure PBA-B2.

TABLE V
Shift of the Carbonyl Group Stretch Absorption Band in Plasticized Films, Analyzed by FTIR

	Plasticizer concentration		
	20%	40%	60%
PBA-L1	4	1	2
PBA-L2	3	2	2
PBA-L3	3	2	2
PBA-B1	3	2	2
PBA-B2	3	5	4
PBA-B3	3	2	2
PBA-B4	3	4	3
DOP	−4	−3	−2
DEHP	−4	−3	−2

Values given are shift measured in cm^{-1}.

Films plasticized with PBA-B2 and PBA-B4 show in accordance with other results (tensile testing, surface composition, and degree of crystallinity) largest shifts at 40 wt % plasticizer. At 20 wt % PBA, most of the films have been shown to be practically amorphous by OM (see below), and a large shift of the carbonyl group stretch absorption band thus indicates good miscibility and low crystallinity.

Film crystallinity

Optical microscopy and visual transparency

To study differences in the crystalline structure of solution cast films, OM was applied. Among the films containing 20 wt %, only films plasticized with PBA-B2 showed a visual presence of crystals. These crystals were small and evenly spread out throughout the film as can be seen in Figure 4. This finding is in good agreement with the tensile testing results where films plasticized with PBA-B2 were the only films to show an elastomeric stress–strain behavior at 20 wt % plasticizer. The small and well-dispersed crystals are proposed to work as physical crosslinks in the amorphous matrix, resulting in an elastomeric material. Other films containing 20 wt % plasticizer were all smooth and visually crystal free with the exception of films plasticized with PBA-B4, which exhibited a somewhat rough surface.

In the case of 40 wt % plasticizer, all films containing polymeric plasticizer showed crystalline domains to some extent. In accordance with tensile testing results, morphological differences seemed more correlated to whether the polyester plasticizer was linear or branched rather than to the molecular weight of the polyester. Exception from this statement must again be made for films plasticized with PBA-B4, which also at this plasticizer concentration exhibited a somewhat rough film surface. Films containing polyesters with a higher degree of branching, i.e., films containing PBA-B1 and PBA-B2, showed large crystal structures
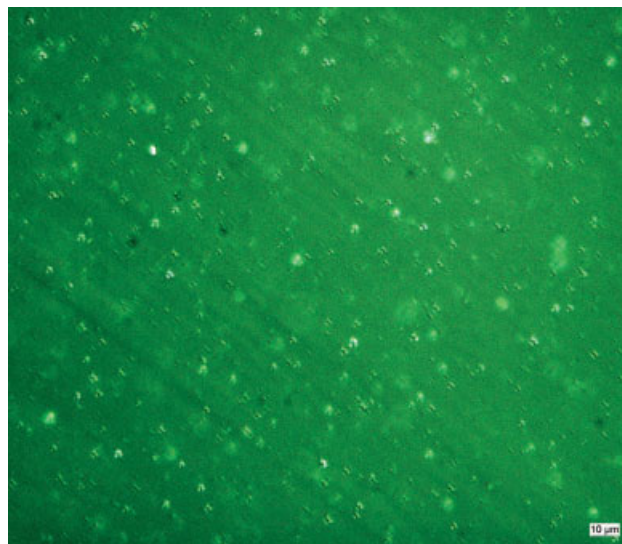

Figure 4 Nonpolarized light optical micrograph of solution cast film plasticized with 20 wt % PBA-B2. The scale bar is equal to 10 μm.

dispersed in the amorphous matrix, see Figures 5 and 6. Tensile testing results presented in the previous section showed that films plasticized with PBA-B1 and PBA-B2 displayed the largest elongation at break, and the correlation suggests that these larger crystals dispersed in the amorphous matrix form a structure similar to that of elastomers. Films plasticized with a less branched polyester, PBA-B3, showed a different crystal structure with smaller, more tightly packed crystals, see Figure 7, and in correlation, a lower elongation at break.
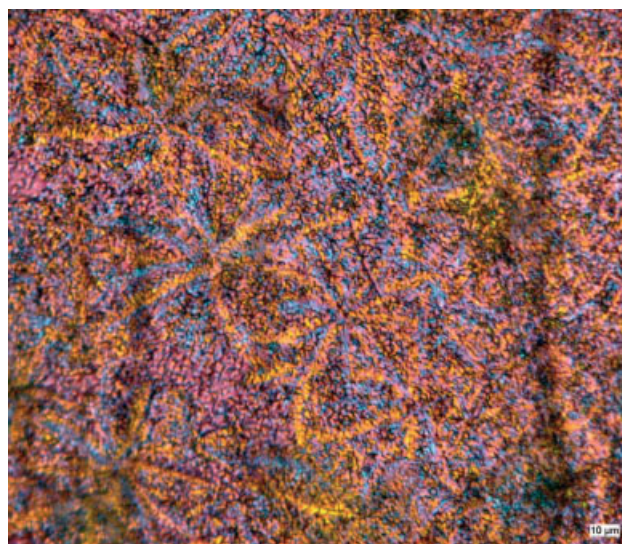

Figure 5 Polarized light optical micrograph of solution cast film plasticized with 40 wt % PBA-B1. The scale bar is equal to 10 μm.
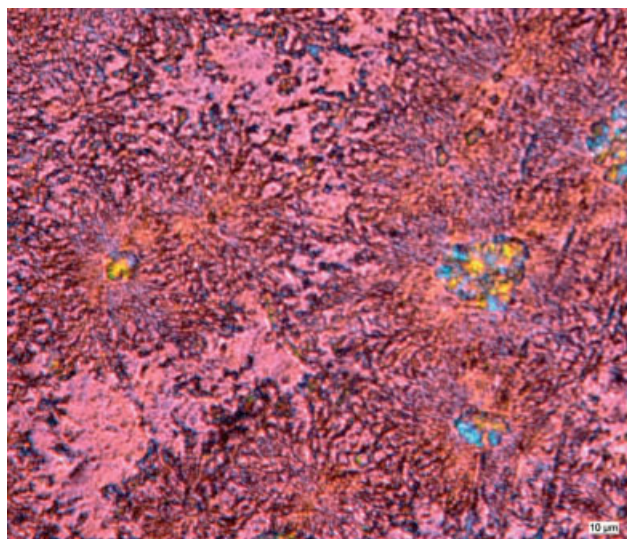
Figure 6 Polarized light optical micrograph of solution cast film plasticized with 40 wt % PBA-B2. The scale bar is equal to 10 μm.

Among the films plasticized with linear polyesters a small difference can be noticed between films containing PBA-L2 *vs*. PBA-L1 and PBA-L3. PBA-L2, with intermediate molecular weight, showed a somewhat larger crystalline structure than that of PBA-L1 and PBA-L3 and in correlation also , to some extent, a larger elongation at break. At 60 wt % plasticizer, all films containing polymeric plasticizer showed a densely packed crystalline structure. Films plasticized with traditional plasticizers DEHP and DOP showed no crystals regardless of the plasticizer concentration, and visual transparency was in good agreement with
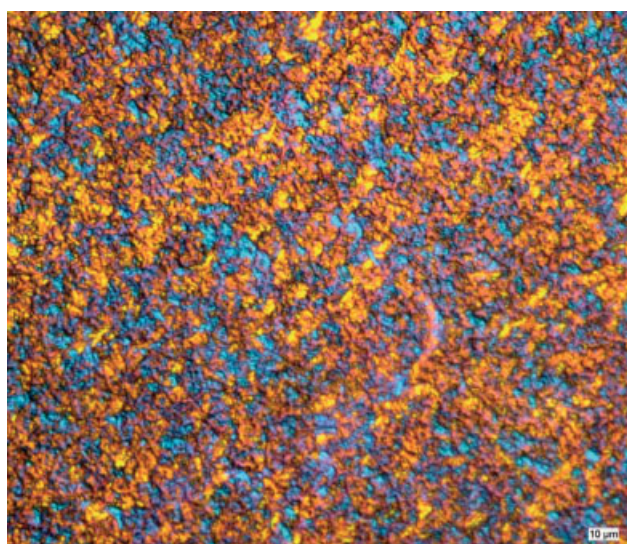

Figure 7 Polarized light optical micrograph of solution cast film plasticized with 40 wt % PBA-B3. The scale bar is equal to 10 μm.
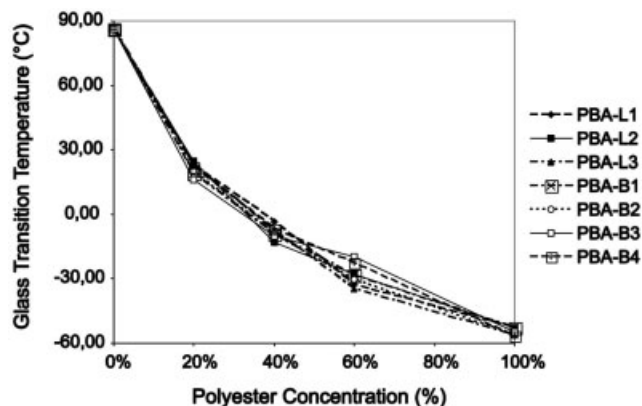

Figure 8 Glass transition temperature (°C) dependence on polyester concentration in PVC/PBA films.

optical micrographs, i.e., showing an increasing transparency with decreasing crystal density.

Differential scanning calorimetry

Glass transition temperature and degree of crystallinity of the solution cast films were measured by differential scanning calorimetry (DSC). The existence of a single glass transition temperature is a well-recognized proof of miscibility in polymer blends. In Figure 8 the recorded glass transition temperatures are plotted as a function of polyester concentration in the cast PVC/PBA films. The values measured for pure PBA were slightly higher than that of the earlier recorded[29] but the values for the analyzed PVC/PBA films were in good agreement with values reported by Ziska et al. in 1981.[14] The presence of a composition-dependent single glass transition temperature in analyzed blends is thus another indication of miscibility between PVC and the synthesized PBA. However, the broader transition widths observed in analyzed blends compared with those of pure polymers, along with the presence of a crystalline polyester phase, indicate that there is only partial miscibility between the two components.

As earlier reported for both the PVC/PCL system[11,30–32] and for PVC/PBA,[14] some of the PVC/PBA blends did not form a totally amorphous film but a two-phase miscible PVC/PBA system. DSC was therefore also used to calculate the amount of crystalline PBA in the different PVC/PBA films. Figure 9 shows the degree of crystallinity as a function of polyester concentration in prepared blends. Degree of crystallinity was calculated by dividing the measured normalized heat of fusion by the theoretical value for a 100% crystalline PBA sample, 135.0 J/g.[34] Most of the blends showed a minimum degree of crystallinity at 40 wt % plasticizer, but the composition dependence of crystallinity was most prominent for films plasti-
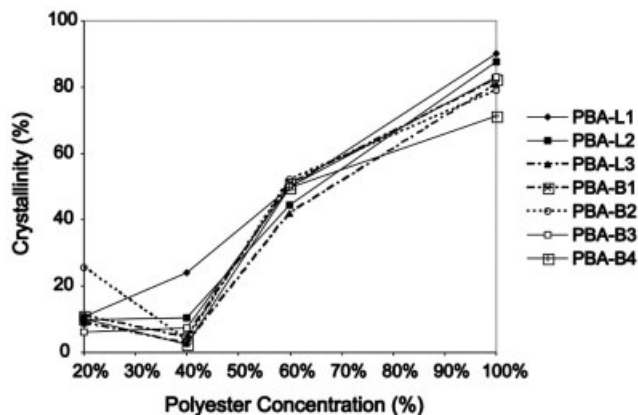
Figure 9 Influence of polyester concentration on degree of crystallinity (%) in PVC/PBA films.

cized with PBA-B2. A lower degree of crystallinity and an indication of a crystalline structure more similar to that of elastomers via larger elongations at break for branched PBA compared with linear PBA was also seen by Han et al.[29] when they characterized solution cast films of pure PBA.

CONCLUSIONS

PBA formed a semimmiscible two-phase system with PVC, where the amorphous part exhibited a single glass transition temperature. Mechanical properties, glass transition temperature, and morphology of PVC/PBA blends depended on molecular weight, degree of branching, and blend composition. Desirable mechanical properties were achieved at a 40 wt % PBA concentration. Branching enhanced the plasticizing efficiency of the polyester plasticizer in terms of greater elongation and improved miscibility.

References

1. Latini, G.; De Felice, C.; Verrotti, A. Reprod Toxicol 2004, 19, 27.
2. Tickner, J. A.; Schettler, T.; Guidotti, T.; McCally, M.; Rossi, M. Am J Ind Med 2001, 39, 100.
3. European Commission Health & Consumer protection directorate-general, Directorate C-Scientific Opinions, C2. Opinion on Medical Devices Containing DEHP plasticized PVC; Neonates and Other Groups Possibly at Risk from DEHP Toxicity. 2002. Doc.SANCO/SCMPMD/2002/0010:final.
4. Hill, S. S.; Shaw, B. S.; Wu, A. H. B. Clin Chim Acta 2001, 304, 1.
5. Latini, G.; De Felice, C.; Presta, G.; Del Vecchio, A.; Paris, I.; Ruggieri, F.; Mazzeo, P. Environ Health Persp 2003, 111, 1783.
6. Kleinsasser, N. H.; Harréus, U. A.; Kastenbauer, E. R.; Wallner, B. C.; Sassen, A. W.; Staudenmaier, R.; Rettenmeier, A. W. Toxicol Lett 2004, 148, 83.
7. Postle, M.; Corden, C.; van den Berg, M.; Sanderson, T. Final Report Prepared for European Commission Directorate-General Enterprise. 2000, July. Contract no ETD/99/502498.
8. Krauskopf, L. G. J Vinyl Addi Techn 2003, 9, 159.
9. Pal, S. N.; Ramani, A. V.; Subramanian, N. J Polym Eng Sci 1992, 32, 845.
10. Chiu, F. -C.; Min, K. Polym Int 2000, 49, 223.
11. Coleman, M. M.; Zarian, J. J Pol Sci 1979, 17, 837.
12. Prud'homme, R. E. Polym Eng Sci 1982, 22, 90.
13. Choe, S.; Cha, Y. -J.; Lee, H -S.; Yoon, J. S.; Choi, H. J. Polymer 1995, 36, 4977.
14. Ziska, J. J.; Barlow, J. W.; Paul, D. R. Polymer 1981, 22, 918.
15. Oriol-Hemmerlin, C.; Pham, Q. T. Polymer 2000, 41, 4401.
16. Shah, B. L.; Shertukde, V. V. J Appl Pol Sci 2003, 90, 3278.
17. Ferruti, P.; Mancin, I.; Ranucci, E.; De Felice, C.; Latini, G.; Laus, M. Biomacromolecules 2003, 4, 181.
18. Czuba, L. Medical Device & Diagnostic Industry Magazine 1999, April.
19. Messori, M.; Toselli, M.; Pilati, F.; Fabbri, E.; Fabbri, P.; Pasquali, L.; Nannarone, S. Polymer 2004, 45, 805.
20. Jayakrishnan, A.; Sunny, M. C. Polymer 1996, 37, 5213.
21. Gibbons, W. S.; Patel, H. M.; Kusy, R. P. Polymer 1997, 38, 2633.
22. Garton, A.; Aubin, M.; Prud'homme, R. E. J Pol Sci Pol Lett 1983, 21, 45.
23. Varnell, D. F.; Moskala, E. J.; Painter, P. C.; Coleman, M. M. Pol Eng Sci 1983, 23, 658.
24. Hallam, H. E. Infra-Red Spectroscopy and Molecular Structure. Elsevier: Amsterdam, 1963, Chapter XII.
25. Garton, A. Pol Eng Sci 1983, 23, 663.
26. Choi, J -S.; Kwak, S. -Y. Polym Matr Sci Eng 2004, 90, 449.
27. Kwak, S.-Y.; Choi, J.-S. United States Patent 2004; Patent No. 6,747,092.
28. Hakkarainen, M. Polym Degrad Stab 2003, 80, 451.
29. Han, Y. K.; Um, J. W.; Im, S. S.; Kim, B. C. J Polym Sci Pol Chem 2001, 39, 2143.
30. Clark, M. B., Jr.; Burkhardt, C. A.; Gardella, J. A., Jr. Macromolecules 1991, 24, 799.
31. Cañavate, J.; Pagès, P.; Rodriguez, M. J.; Pérez-Folch, J.; Carrasco, F.; Colom, X. J Polym Mater 2001, 18, 33.
32. Penco, M.; Sartore, L.; Bignotti, F.; Rossini, M.; D'Amore, A.; Fassio, F. Macromol Symp 2002, 180, 9.
33. Karal, O.; Hamurcu, E. E.; Baysal, B. M. Polymer 1997, 38, 6071.
34. Nikolic, M. S.; Djonlagic, J. Polym Degrad Stab 2001, 74, 263.