Polym. Bull. (2010) 65:589–598
DOI 10.1007/s00289-010-0271-4

ORIGINAL PAPER

Poly(vinyl chloride) plasticized with succinate esters: synthesis and characterization

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Received: 21 September 2009 / Revised: 18 December 2009 / Accepted: 28 March 2010 /

Abstract Phthalates pose adverse health effects due to their propensity to leach and the most common, di(2-ethylhexyl) phthalate (DEHP) and di-*n*-octyl phthalate (DOP), are petroleum-based. Conversely, di-esters, succinates are biobased (produced from fermentation of biomass), biodegradable, and therefore potential sustainable replacements for phthalates. A series of succinates, di-octyl succinate (DOS), di-hexyl succinate (DHS), di-butyl succinate (DBS), and di-ethyl succinate (DES), were mixed with poly(vinyl chloride) (PVC). The interaction of the plasticizer ester carbonyl with PVC shows an average $-5\ \text{cm}^{-1}$ shift of the carbonyl absorbance peak energy. The glass transition temperatures (T_g), were monitored by differential scanning calorimetry and dynamic mechanical analyses. The T_gs of DOS and DHS plasticized PVC were significantly lower than DOP plasticized PVC at a lower percent mass. On the other hand, PVC plasticized with either DBS or DES exhibited a similar trend in lowering the T_g as that of DOP plasticized PVC.

Keywords PVC · Succinate · Plasticizer · Biobased

Introduction

Plasticizers are used extensively to provide flexibility and ease of processing for poly(vinyl chloride) (PVC), and other polymers including natural rubber, cellulose, poly(vinyl butyral), and poly(vinyl acetate) [1]. As much as 40% by weight of a PVC product can be non-covalently bonded plasticizer. Due to this lack of covalent bonding, plasticizers can leach out of products into the application environments [2].

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Millions of pounds of plasticizer are consumed each year. In the United States about 70% are phthalate esters. Of the 25 different phthalate esters, di(2-ethylhexyl) phthalate (DEHP) and di-*n*-octyl phthalate (DOP) are the most commonly used with PVC. Phthalates and related compounds are linked to adverse effects in the liver, reproductive system, kidney, lung, and heart. [3] The environmental contamination and health hazards that occurs from numerous applications including toys, food containers, household plumbing, plastic waste, and chemical production waste has given impetus for the replacement of phthalates [2–5]. In addition to the health and environmental concerns, phthalate plasticizers are petroleum-derived. Petroleum-based processes generate greenhouse gases, which contribute to a myriad of other environmental issues [5]. These have diminished and continue to diminish the market desirability of PVC.

Biodegradable, benign, and non-petroleum-based plasticizers with properties similar to or better than the phthalates offer a desirable alternative, if they can be economically competitive. These compounds can be prepared from various carboxylic acids. Biobased processes that are more eco-friendly than traditional petrochemical processes, consume less energy, generate less waste, and reduce the dependence on petroleum [4]. Traditionally, the expensive production cost of these carboxylic acids using biocatalysts has been a roadblock for commercialization [6]. However, recent proliferation of efficient biobased technology has bridged the cost gap for potential production of effective, benign, biobased plasticizers using naturally derived end products [4]. Citric-based plasticizers are on the market and an economical method has been developed for producing succinic acid in a clean and effective manner via aerobically grown bacteria fermentation of biomass containing sugars (consisting of five or six carbon atoms) [4, 7]. Additionally, short chain alcohols including ethanol and butanol can be produced through biomass fermentation processes [4]. Longer chain alcohols, such as 1-octanol, can be prepared with the use of enteric bacteria, *E. coli*, and potassium salts [8]. These technological advances have given impetus to use succinates with varying lengths of alkoxyl chains as biobased plasticizers for PVC.

Succinic and citric replacements for phthalates have precedence for being biobased and benign. Citric acid and succinic acid are components of the Kreb's cycle [9]. The presence of a chemical in a metabolic process implies that the same chemical can potentially be produced in an efficient manner in bulk quantities [7]. Since metabolic pathways for chemical formation are usually reversible by another metabolic mechanism, citric and succinic acids should be less toxic [9]. Esters derived from naturally available citric acid and alcohols have been investigated as possible benign alternatives to phthalate-based plasticizers with varying degrees of success [10]. For example, the ester of citric acid, with the exception of acetyltributyl citrate, is currently being used in food wraps and blood bags [10, 11]. Acetylbutyl citrate has been produced for specific nontoxic applications. However, it was later shown to be more toxic than DEHP [11]. Although citrates are gaining market appeal as replacements for phthalate plasticizers, they offer minimal technical advantages [1] and have not replaced phthalates as the dominant market players.

Succinate di-esters have the potential for biobased production due to the upsurge of sustainable technology. There is limited precedence in the literature for succinate-based plasticizers. For example, diesters of di-acids with varying numbers of methylene units and varying lengths of the alkoxy groups have been evaluated as plasticizers. These variations affect polymer compatibility, plasticizing ability, and mechanical properties [12]. These esters were prepared by using petroleum-based starting materials and consequently, were not considered viable alternatives to phthalates [6]. We report herein the preparation of a series of succinate diesters and their efficacy as plasticizers for PVC.

Experimental

PVC, ($M_w = 97{,}000$), was obtained from Sigma-Aldrich. Succinic acid was obtained from Eastman Organic Chemicals. All other reagents, including 1-octanol, 1-hexanol, di-ethyl succinate (DES), and di-butyl succinate (DBS), were purchased from Sigma-Aldrich and used as received. All solvents were ACS reagent grade. Commercially unavailable di-octyl succinate (DOS) and di-hexyl succinate (DHS) were synthesized following previously established methods [13].

Nuclear magnetic resonance (NMR) spectra (^{1}H and ^{13}C) were recorded using a Varian Mercury Plus 300 MHz NMR Spectrometer using deuterated trichloromethane as the solvent. All NMR chemical shifts are reported in parts per million (δ) relative to tetramethylsilane standard (TMS $\delta = 0.00$). FTIR spectra were obtained on a Nicolet IR 584 spectrometer at room temperature using a NaCl disk, a resolution of 2 cm^{-1}, and 64 scans. Differential Scanning Calorimetry (DSC) was performed on a Perkin-Elmer Diamond DSC instrument at a heating rate of 10 °C/min. A constant flow of nitrogen gas was used during the measurements. The mass spectra of samples were obtained using electrospray ionization mass spectrometer (ESI-MS) operating in a positive ion mode. Dynamic mechanical analysis (DMA) was performed on a TA Instruments Q800 DMA with gas cooling accessory (GCA) to observe the α-transitions of the samples under investigation. Rectangular polymer samples of geometry 20 (l) × 6 (w) × 0.1 (t) mm were tested in the film tension mode with a preload force of 0.05 N and a force track of 120%. The samples were cooled with liquid N_2 and scanned from −100 to 100 °C at a ramp rate of 2 °C, frequency of 1 Hz, and amplitude of 15 μm. Storage modulus and loss modulus were measured as a function of temperature and the corresponding tan δ was calculated.

Synthesis of DOS

Succinic acid (9.37 g, 0.0794 mol), 1-octanol (25.0 mL, 0.159 mol, excess), and a catalytic amount of aqueous concentrated H_2SO_4 were mixed in a 500 mL round-bottomed flask fitted with a magnetic stir bar and a Dean-Stark trap. Toluene (125 mL) was added to the reaction vessel. The water produced as a by-product of the reaction was removed by azeotropic distillation with toluene. The reaction vessel was heated using an external oil bath, and the reaction was allowed to continue under reflux for 18 h. After the completion of the reaction, toluene and excess 1-octanol were removed at reduced pressure using a rotary evaporator. The product, a clear, colorless, oily liquid was obtained in 70% yield.

^{1}H NMR ($CDCl_3$) δ 0.88 (6H, t, $J = 7.5$ Hz), 1.29 (20H, m), 1.62 (4H, m), 2.62 (4H, s), 4.08 (4H, t, $J = 6$ Hz). ^{13}C NMR (CCl_3D) δ 14.0, 22.6, 25.8, 28.5, 29.2, 31.7, 64.9, 172.3.

ESI-MS (m/z): 343 $[M + H]^+$.

IR, Neat (cm^{-1}) 1161, 1739.

Synthesis of DHS

Succinic acid (10.18 g, 0.0862 mol), 1-hexanol (25.0 mL, 0.199 mol, excess), and a catalytic amount of concentrated H_2SO_4 were used to synthesize DHS using the same procedure described above. The product, a clear, colorless, oily liquid was obtained in 78% yield.

^{1}H NMR ($CDCl_3$) δ 0.89 (6H, t, $J = 6.0$ Hz), 1.30 (12H, m), 1.62 (4H, m), 2.62 (4H, s), 4.08 (4H, t, $J = 7.5$ Hz). ^{13}C NMR ($CDCl_3$) δ 13.9, 22.5, 25.5, 28.5, 29.1, 31.4, 64.8, 172.3.

ESI-MS (m/z): 309 [M + Na], 595 [2 M + Na].

IR, Neat (cm^{-1}) 1162, 1739.

Preparation of plasticized PVC films

To prepare the films, PVC (0.75 g) and the desired amount of plasticizer were added to a 20 mL vial, followed by the addition of tetrahydrofuran (THF) (8–10 mL). The mixture was agitated until a homogenous solution was obtained. For DSC and DMA analyses, films were obtained by casting this solution on a glass plate. Residual THF was removed under vacuum at room temperature for 8 h.

Results and discussion

Film characteristics

The effects of these biobased plasticizers at varying weight percents with PVC were evaluated. Typical flexible PVC formulations (Table 1) were chosen to assess the

Table 1 Formulations for preparing plasticized PVC films

	Formulation						
	1	2	3	4	5	6	7
PVC (g)	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Plasticizer (g)	0.679	0.450	0.285	0.160	0.107	0.061	0.019
Plasticizer (wt%)	47.5	37.5	27.5	17.5	12.5	7.5	2.5

properties of plasticized PVC films, in the absence of other commonly used additives [14].

Each of the films was approximately 0.1 mm thick. The PVC films plasticized with DOP, DOS, DHS, DES, and DBS were all clear and colorless. Each of the films became more flexible with increasing plasticizer concentration. At low concentrations, (DES and DBS concentrations of 2.5–37.5% and DOP, DOS, and DHS concentrations of 2.5–27.5%), the films appeared more flexible than unplasticized PVC, but they were not fingernail creasable. However, PVC films plasticized with higher concentrations of plasticizers, (DES and DBS concentration of 47.5% and DOP, DOS, and DHS concentrations of 37.5 and 47.5%), were more flexible and fingernail creasable. From these qualitative observations, it was apparent that the succinates with short (ethyl and butyl) chains are less efficient than the succinates with longer (hexyl and octyl) chains and DOP in plasticizing PVC. To further evaluate and quantify these observations, FTIR, DSC, and DMA analyses of the samples were performed.

Infrared spectroscopy

Frequency shifts in the FTIR spectrum indicates specific molecular interactions between plasticizer and polymer—essential for compatibility [15]. The hydrogen atom attached to the chlorine-bearing carbon atom of PVC is slightly acidic due to the high electronegativity of the chlorine atom. The oxygen atom of the carbonyl group of an ester group is electron rich, allowing for weak acid–base interactions between PVC and the ester group of a plasticizer [15]. For example, the absorbance of the carbonyl group of dibutyl phthalate shifts to a lower frequency when it is blended with PVC [16]. Similar observations in frequency shifts of the carbonyl band position have been reported for a 50:50 weight percent blend of ethylene/*N*,*N*′-dimethylacrylamide with PVC [15].

The absorbance due to the carbonyl groups of the succinates appears between 1737 and 1739 cm^{-1} (Table 2). As an example, the spectra for pure DHS and DHS mixed with PVC (7.5%) have a 6 cm^{-1} shift for the carbonyl peak (Fig. 1). For each plasticizer, the absorbance shifts to a lower frequency upon blending with PVC. An examination of these data indicates the following. First, the average shift of the carbonyl absorbance of all four succinates is -5 cm^{-1}, which is in agreement with observations for the PVC–DOP system [14]. This suggests strongly that the

Table 2 FTIR frequency shifts with changing weight percent of plasticizers

Plasticizer	Pure plasticizer C=O ester (cm^{-1})	7.5% Plasticizer Δv (cm^{-1})	27.5% Plasticizer Δv (cm^{-1})	47.5% Plasticizer Δv (cm^{-1})
DOP	1,728	−6	−4	−3
DOS	1,739	−8	−5	−5
DHS	1,739	−6	−6	−4
DBS	1,737	−5	−5	−5
DES	1,737	−5	−5	−5

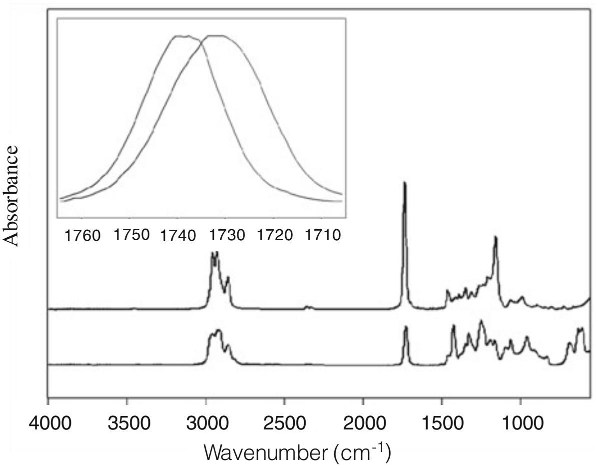

Fig. 1 FTIR spectra of DHS (*top trace*) and 7.5% DHS plasticized PVC (*bottom trace*); *Inset* (1710–1760 cm^{-1})

magnitude of interactions of succinate-based plasticizers and DOP with PVC are similar. Second, a parallel trend is observed in the frequency shifts with changing weight percent of DOS, DHS, and DOP. With increasing weight percent of these three plasticizers, it is likely that a saturation point is reached for effective interactions due to similar steric crowding by the long alkoxy groups. This trend is not observed for succinates with shorter alkyl chains (DES and DBS)—the frequency shift should remain unchanged with increasing plasticizer content, as long as sites for interaction on the PVC backbone are available. Our data confirms this conjecture.

DSC

The T_g of un-plasticized PVC measured by DSC was 86 °C, consistent with reported literature values [10, 17]. Data from FTIR analyses suggest that succinates interact with the PVC chains. This lowers inter-chain interactions and increases free volume. Consequently, the glass transition temperature decreases. The extent of this decrease is dependent on polymer inter-chain attractions and increased free volume. Free volume increase is a function of the amount, the structure, and the nature of interaction of the succinates with the PVC chains. An examination of the DSC thermograms of plasticized PVC with increasing weight percents of DHS (Fig. 2) indicates that the T_g values decrease and the transition range broadens with increasing DHS concentrations. Similar trends were obtained with the other succinates (DOS, DBS, and DES) and DOP plasticized PVC (Fig. 3). With increasing plasticizer concentration, the T_g value decreases steadily until a specific concentration where the T_g quickly drops below 0 °C and then below the instrument threshold of −60 °C (Table 3). An examination of the data indicates that DOS and DHS plasticized PVC exhibit a significant drop in the glass transition temperature from 27.5 to 37.5%. This

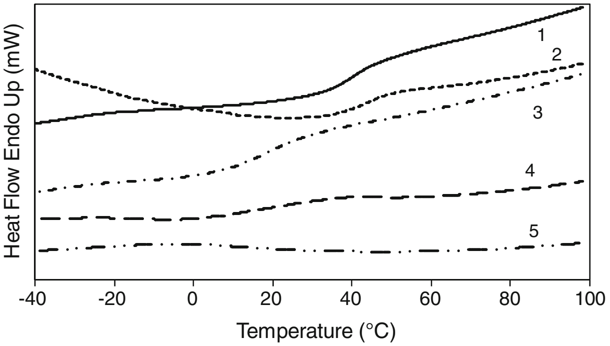

Fig. 2 Glass transitions of PVC films plasticized with DHS in weight percents of 2.5% (*1*), 7.5% (*2*), 12.5% (*3*), 17.5% (*4*), and 27.5% (*5*)

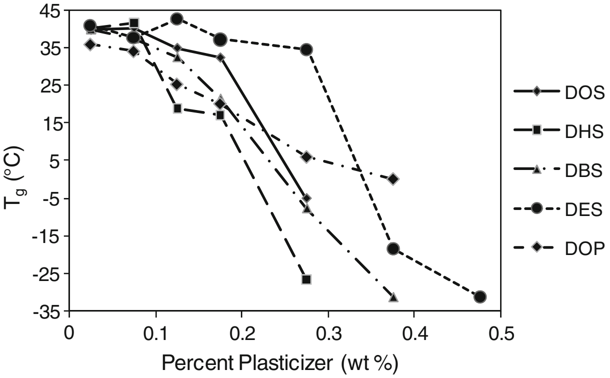

Fig. 3 The glass transition temperatures of plasticized PVC films as a function of plasticizer concentration

dramatic drop is observed for DBS plasticized PVC from 37.5 to 47.5%. DES plasticized PVC has a T_g value above −60 °C at significantly higher plasticizer concentration (47.5%). These observations suggest that the size of the alkoxy group plays a critical role in controlling the available free volume. Furthermore, the observed T_g for PVC films plasticized with 2.5 and 7.5% DOS, DHS, DBS, and DES decreased from 86 to 40 °C (Fig. 4), similar to DOP plasticized PVC.

DMA

PVC exhibits a primary (α) and a secondary (β) relaxation [17]. The α-relaxation, the T_g, results from the segmental molecular motions, and the β-relaxation is a consequence of the local motions of small groups in the PVC chain [18]. The presence of plasticizer decreases T_g, therefore shifting the modulus and tan δ curve transitions to lower temperatures and broadening the tan δ peaks [19]. Consistent with the trend observed from data obtained from DSC experiments, increasing DOS concentration lowers the tan δ peak temperature, and increases the peak width

Table 3 Glass transition temperatures of PVC films

	Glass transition temperature (°C)						
Sample wt%:	2.5	7.5	12.5	17.5	27.5	37.5	47.5
DOP	36	34	25	20	6	0	–
DOS	40	40	35	32	−5	–	–
DHS	40	42	19	17	−27	–	–
DBS	40	37	32	21	−8	−31	–
DES	41	38	43	37	34	−19	−31

–, Not observed

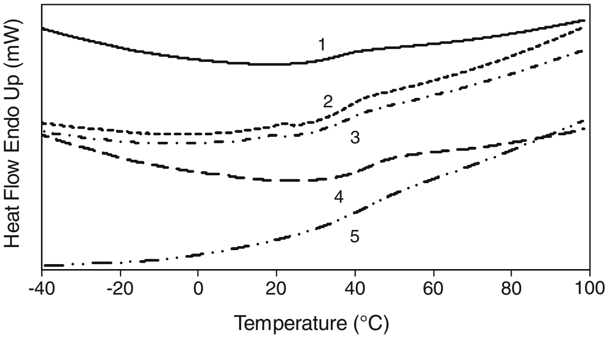

Fig. 4 Glass transitions of PVC films plasticized with 7.5% by weight of DOP (*1*), DES (*2*), DBS (*3*), DHS (*4*), and DOS (*5*)

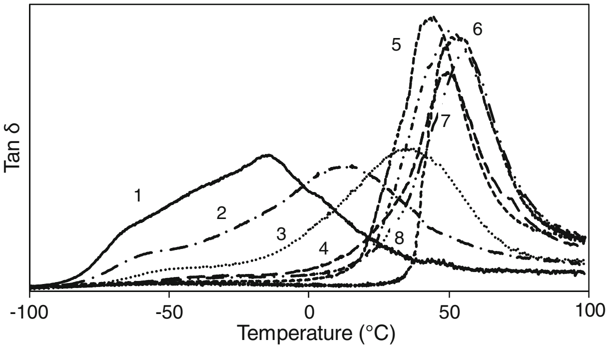

Fig. 5 Tan δ peaks for pure PVC film and PVC films plasticized with 47.5% (*1*), 37.5% (*2*), 27.5% (*3*), 17.5% (*4*), 2.5% (*5*), 7.5% (*6*), 12.5% (*7*), and pure PVC (*8*) by weight percent DOS

(Fig. 5). The peak broadening is observed regardless of the plasticizer concentration, while the significant decrease in peak temperature is not apparent until more than 17.5% plasticizer is present. Similar to the trends observed from the DSC

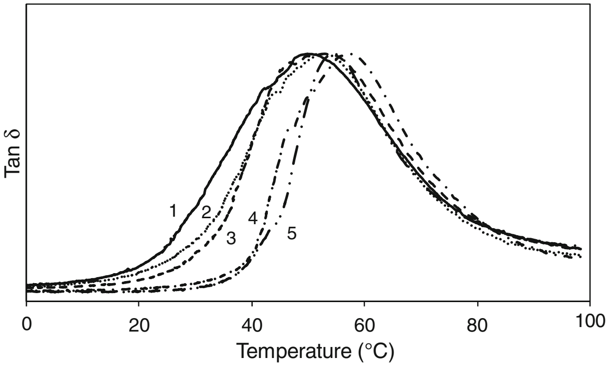

Fig. 6 Tan δ peaks normalized for pure PVC film and PVC films plasticized with 7.5% by weight DOS (*1*), DOP (*2*), DHS (*3*), DBS (*4*), and DES (*5*)

analyses, an examination of DMA data (Fig. 6) indicates that irrespective of the nature of plasticizers (7.5%), lowering of the glass transition temperatures as well as the broadening of the tan delta peaks could be observed. Furthermore, the modulus values at 25 °C are 3, 10, and 23% greater from the DOS to DOP, DHS, and DBS respectively.

Conclusions

As an alternative to commonly used, petroleum-based phthalates (DEHP and DOP), which pose adverse health effects, a series of biobased succinate esters, DOS, DHS, DBS, and DES, were examined for effectiveness as PVC plasticizers. Succinates with longer alkoxy chains, (DOS and DHS), were shown to be as or more efficient than DOP in plasticizing PVC on a mass percent basis. The succinates with shorter alkoxy chains (DBS and DES) did not appear to achieve a comparable amount of plasticization on a mass percent basis. However, similar results were obtained with higher concentration levels. These results establish all four succinates as potentially biobased, sustainable alternatives to phthalate plasticizers.

Acknowledgments The authors would like to acknowledge early project inputs from Prof. Kris Berglund of Lulea University and Michigan State University and Dr. Dilum Dunuwila from Diversified Natural Products Green Technology Inc. This work was supported by the Research Excellence Fund from Central Michigan University.

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