Oligomeric Isosorbide Esters as Alternative Renewable Resource Plasticizers for PVC

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ABSTRACT: Oligo(isosorbide adipate) (OSA), oligo(isosorbide suberate) (OSS), and isosorbide dihexanoate (SDH) were synthesized and evaluated as renewable resource alternatives to traditional phthalate plasticizers. The structure of the synthesized oligomers was confirmed by nuclear magnetic resonance spectroscopy (^{1}H- and ^{13}C-NMR), and molecular weight was determined by size exclusion chromatograph. The plasticizers were blended with poly(vinyl chloride) (PVC), and the miscibility and properties of the blends were evaluated by differential scanning calorimetry, fourier transform infrared spectroscopy, tensile testing, and thermogravimetry. Especially the blends plasticized with SDH had almost identical properties with PVC/diisooctyl phthalate (DIOP) blends. The blends containing OSA and OSS plasticizers, based on dicarboxylic acids, had somewhat lower strain at break but higher stress at break and better thermal stability compared to the PVC/DIOP or PVC/SDH blends. All the synthesized isosorbide plasticizers showed potential as alternative PVC plasticizers. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 2400–2407, 2011

Key words: poly(vinyl chloride); PVC; renewable resources; blends; polyesters; isosorbide

INTRODUCTION

Phthalate esters, widely used as poly(vinyl chloride) (PVC) plasticizers, and their possible health and environmental impacts have been a subject of debate for years. The toxicity of phthalates was studied by researchers as early as in 1940s.[1] Since 1990s, various negative effects of phthalates on animals were revealed and caused public concerns. Adverse effects of phthalates on animals' liver, heart, kidneys, lungs, and other organs have been concluded.[1] On the basis of the animal experiments, it was also predicted that humans may experience reduced sperm counts, histological changes in testes, and reduced fertility as a result of exposure to some phthalates.[2] Since 1999, six phthalate plasticizers are forbidden to be used in child care-articles and toys that can be placed in the mouths of children under the age of three in Europe. Later, three of these plasticizers were forbidden to be used in any toys and child care products within Europe. However, due to the low price and good performance, di(2-ethylhexyl)phthalate (DEHP) and other phthalate plasticizers are still widely used in other applications. A recent review summarizes previous results on the migration of phthalate esters from PVC to different environments.[3] The fate of phthalate esters in environments such as soil,[4] marine ecosystem,[5] and indoor air[6] has also been studied. Janjua et al.[7] showed that some of the phthalate esters have the ability to penetrate human skin rapidly. Models to predict the emission behaviors of DEHP from polymer were built by Xu and Little,[8] and the results showed the high possibility of DEHP transfer from air to human skin.

Many alternative plasticizers have been developed. However, no other plasticizer has been able to compete with phthalates on a larger scale. The most common PVC plasticizers are still different phthalate esters. Polymeric plasticizers such as poly(butylene adipate) (PBA) are used in many food-contact applications to prevent plasticizer migration.[9] Lindström and Hakkarainen[10] designed improved PBA plasticizers, by introducing different degrees of branching and different end groups. Highly branched PBA was not a good alternative as a PVC plasticizer because of rather poor miscibility and higher hydrophilicity.[11] However, slightly branched PBA exhibited better plasticizing efficiency and migration resistance compared to the linear and highly branched ones.[12,13] Polycaprolactones and their copolymers have also been considered as alternatives to phthalate plasticizers. Choi and Kwak[14] reported the use of

hyperbranched poly(ε-caprolactone) (HPCL) as an alternative for DEHP, and found that HPCL showed a similar plasticizing efficiency than DEHP but had much better migration resistance.

An additional options to decrease the negative impacts of PVC plasticizers is to develop "green" plasticizers from renewable resources.[15] Different carboxylic and dicarboxylic acids and diols such as isosorbide are examples of renewable resource monomers that are being predicted for large-scale production in the future.[16] Polyesters,[17–19] polyamides,[20] and polycarbonates[21] have already been synthesized from isosorbide. Our aim was to develop renewable resource plasticizers with good plasticizing efficiency and miscibility with PVC. The replacement of the aliphatic alcohols used in the most common polyester or oligoester plasticizers with the cyclic isosorbide leads to a structure more similar to traditional phthalate plasticizers, which could lead to improved blend properties. In addition, the more bulky structure of isosorbide is expected to prevent plasticizer crystallization, which is a common problem with polyester plasticizers.

EXPERIMENTAL

Chemicals

Isosorbide (98%), adipic acid (AA) (99%), hexanoic acid (HA) (99%), suberic acid (SA) (≥98%), dimethyl adipate (DMA) (99+%), and dibutyl tin oxide (98%), which was used as catalyst for all reactions, were purchased from Sigma-Aldrich Chemie GmbH (Steinheim, Germany) and used as received. Tetrahydrofuran (THF, HPLC grade), methanol (HPLC grade), and chloroform (HPLC grade) were obtained from Fisher Scientific (UK Limited), and ethanol (96%) was from VWR International (Leuven, Belgium). Diisooctyl phthalate (≥99%) was purchased from Sigma-Aldrich Chemie GmbH (Steinheim, Germany) and used as received.

Synthesis of the oligomeric plasticizers

Three different plasticizers were synthesized: oligo (isosorbide adipate) (OSA), oligo(isosorbide suberate) (OSS), and isosorbide dihexanoate (SDH). OSA plasticizers with different molecular weights and end groups were synthesized by prolonging the reaction time or using DMA as a monomer instead of AA. To synthesize OSA, isosorbide, AA, and dibutyl tin oxide were added into three necks round bottom reaction vessel in molar ratio 1 : 1.05 : 0.12. Then the reaction vessel with Allihn condenser was heated to 130°C in the silicon oil bath under nitrogen gas for 2 h and then cooled down to room temperature under nitrogen. After the first step, Allihn con-

denser was changed to the distillation system. For the second step with distillation the reaction temperature was raised to 180°C under nitrogen gas and kept for 3 h. The water formed in the reaction was distilled from the vessel continuously. The whole system was cooled down to room temperature after the reaction was finished; the material inside the reaction vessel was dissolved in chloroform and moved to a separatory funnel. The oligomers were precipitated in methanol and collected into flask that was kept in the fume hood without lid until the total weight did not decrease, after which they were sealed for further use. For the synthesis of OSS plasticizer SA was used instead of AA and the temperature of the first reaction step was raised to 150°C because the melting point of SA is around 140°C. The product was first dissolved in ethanol, and the oligomer was precipitated in water. To synthesize SDH, HA was used instead of AA but the molar ratio for isosorbide:HA was 1 : 2.1 because there is only one acid group in hexanoic acid. NaOH solution (pH = 12) was used to dissolve the product, SDH, which was then precipitated in water. In addition, two poly(isosorbide adipates) were synthesized. In the first synthesis DMA was used instead of AA to synthesis OSA-D. For the second synthesis the distillation time was prolonged to 8 h to produce OSA-8H.

Nuclear magnetic resonance

Samples were analyzed by Bruker Avance 400 Fourier transform nuclear magnetic resonance spectrometer (FT-NMR) operating at 400 MHz (^{1}H-NMR and ^{13}C-NMR). The temperature was 25°C and dimethyl sulfoxide-d_6 ((CD_3)$_2$SO) was used as a solvent. 10 to 20 mg of each oligomer was dissolved in 0.5 mL solvent.

Size exclusion chromatography

The molecular weights of all the plasticizers were determined by Viscotek TDA model 301 triple detector array size exclusion chromatography (SEC) apparatus (viscosimeter, refractive index detector, and light scattering detector) equipped with two GMH$_{HR}$-M columns with TSK-gel (mixed bed 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 (THF) 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 using toluene as an internal standard. Columns and detectors were kept at 35°C. 20–30 mg sample was dissolved

in 10 mL THF (with 2 ppm of toluene) and introduced into a small vial for the analysis.

Solution casting

Plasticizer/PVC blend films were prepared by solution casting. Commercial phthalate plasticizer was used for comparison. For each plasticizer, two different films were prepared containing 20 or 40 wt % plasticizer. The total of 2 g of plasticizer and PVC were dissolved in 80 mL tetrahydrofuran (THF) at 40°C. After everything dissolved, the solutions were casted on clean petri dishes and dried at ambient pressure and room temperature for 7 days to evaporate all THF. Then the solid films were taken out and put into vacuum oven for another 7 days after which the films were well packed in aluminum foils and were kept in desiccators for further testing. All the glassware used in solution casting was flushed by compressed air to minimize the presence of dust particles.

Tensile testing

For each film, five or more specimens with a rectangular shape (80×5 mm^2) were prepared by using EP 04/80 $\times$ 5 mm^2 specimen cutter (Elastocon AB, Sweden). Before testing samples were conditioned for 6 days at 23°C and 50% humidity. The thicknesses of specimens were measured by using thickness meter. Then mechanical properties of films were tested by Instron 5566 equipped with pneumatic grips and Instron series IX software (Bristol, United Kingdom). The initial grip separation was 25 mm; crosshead speed was 50 mm/min; and load cell was 100 N. Elongation of testing specimens was calculated from grip separation by the software automatically.

Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) of the synthesized oligomers and films were recorded by Perkin–Elmer Spectrum 2000 FTIR spectrometer (Norwalk, CT) equipped with a single-reflection attenuated total reflectance (ATR) accessory (golden gate) from Graseby Specac (Kent, United Kingdom)

Optical microscopy

Optical microscopy (OM) images with 25 times magnification were taken by Leitz Ortholux POL-BK II optical microscope equipped with a Leica DC 300 camera and processed by Leica IM50 software. Polarized light was used as well to detect possible crystallinity in the films.

Scanning electron microscopy

Ultra-High Resolution FE-SEM (Hitachi S-4800) was used to monitor the surface morphology of all the PVC/Plasticizer films. Sample surfaces were covered by 2 nm thick carbon layer and 2 nm thick gold layer before analysis. Secondary electron detectors were used.

Differential scanning calorimetry

Mettler-Toledo DSC 820 was used to perform differential scanning calorimetry (DSC) analysis. Around 5 mg of each PVC/plasticizer films was enclosed into standard 40 μL aluminum cups. Temperature was raised 5°C/min from 25 to 80°C (to 120°C for pure PVC films) and then decreased to 25°C with same rate. After that the samples were cooled down from 25 to −50°C at rate of 1°C/min, and 0.5°C/min from −50 to −70°C. The temperature was kept constant at −70°C for 10 min then increased from −70 to 120°C at rate of 5°C/min. The whole temperature program was performed under a nitrogen gas flow of 80 mL/min.
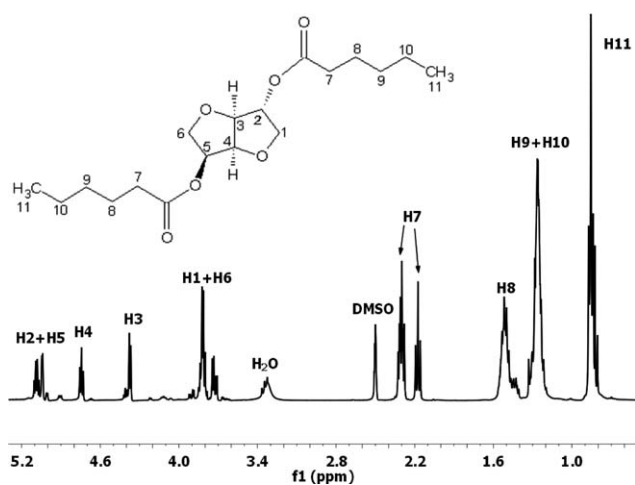
Thermogravimetric analysis

Thermogravimetric analysis (TGA) analyses were performed by Mettler-Toledo TGA/SDTA 851e. Around 10 mg of each blend was put into a 100-μL aluminum cup without lid. Samples were heated at 10°C/min from 30 to 600°C with 50 mL/min oxygen flow in the furnace.

RESULTS AND DISCUSSION

Several isosorbide esters including SDH, OSA, and OSS, were synthesized, characterized, and tested as alternative renewable resource plasticizers for PVC. Miscibility of the blends was evaluated by investigating the intermolecular interactions by FTIR and glass transition temperatures by DSC. Mechanical properties were determined by tensile testing and compared to corresponding PVC/phthalate blends.

The molecular structures of the synthesized plasticizers

The molecular structures of the synthesized plasticizers were confirmed by ^{1}H-NMR and ^{13}C-NMR. The ^{1}H-NMR spectra of SDH is shown as an example in Figure 1. Peaks located in region 3.6–5.2 ppm in this spectra exhibit all the protons from isosorbide function and they are in good agreement with the NMR spectra of other isosorbide compounds reported by Beldi et al.[22] In the ^{1}H-NMR spectra of hexanoic acid, there is only one group of multipeaks at 2.18 ppm, but two groups of multipeaks appeared

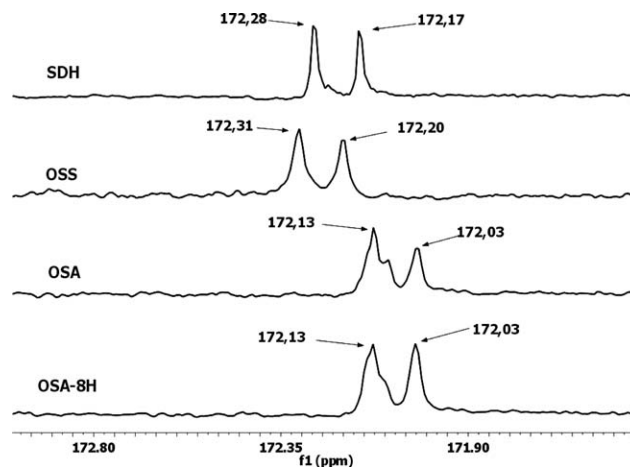**Figure 1** ^{1}H-NMR spectra of SDH using dimethyl sulfoxide-d_6 as solvent.

Figure 2 ^{13}C-NMR spectra showing a comparison of carbonyl group signals for the different plasticizers.

at 2.18 ppm and 2.30 ppm in the ^{1}H-NMR spectra of SDH. A similar situation was also seen in OSA and OSS spectra. This was deduced to the sterically different hydrogen atoms originating from the reaction of the acid groups with the two different alcohol groups in the isosorbide and not to residual hexanoic acid as the hydrogen in the acid group of hexanoic acid were not detected in the NMR spectra of SDH. This hydrogen was clearly seen in the NMR spectra of hexanoic acid monomer. In Figure 2, part of the ^{13}C-NMR spectra are shown to compare the carbonyl groups of different plasticizers. Doublets at around 172 ppm were found for all the synthesized plasticizers, these peaks originate from the carbon at the ester group and the splitting was again attributed to the stereo structure of isosorbide.[23]

Molecular weight of the plasticizers

The molecular weights and polydispersity indexes (PDI) of all the synthesized plasticizers as determined by triple detector SEC and universal calibration are shown in Table I. The PDI and molecular weight for OSA plasticizer increased as a function of reaction time. After the same reaction time and conditions, OSA-D had higher molecular weight and slightly lower PDI value compared with OSA probably due to the higher reactivity of dimethyl adipate. The number average molecular weights show that in

the case of OSA most of the products were dimeric meaning that only one of the hydroxyl groups in isosorbide reacted with one adipic acid unit. This is in agreement with ^{1}H-NMR, which showed that there are approximately as many isosorbide and adipic acid units. In the case of OSS and OSA-D, the products were mainly trimeric. In the ^{1}H-NMR spectra of OSS, the ratio of isosorbide function and suberic function is 1 : 1.6, indicating in combination with molecular weight results that most OSS oligomers were trimers containing one isosorbide and two suberic units. In OSA-D ^{1}H-NMR spectra, the number of hydrogen atoms originating from isosorbide groups and from adipic acid groups is almost the same, indicating similar amounts of trimers containing one isosorbide and two adipic unit or two isosorbides and one adipic unit. After the longer reaction time (OSA 8H) somewhat larger oligomers were obtained containing on average two isosorbide and two adipic units on each molecule.

Comparison of mechanical properties of PVC films with different plasticizers

The plasticizing efficiency of the synthesized plasticizers was evaluated by tensile testing of the blends. The tensile stress at break, tensile strain at break, and modulus for the films plasticized with DIOP, SDH, OSA and OSS are compared in Figures 3–5,

TABLE I
Average Molecular Weights and Polydispersity Index for the Synthesized Plasticizers as Determined by SEC

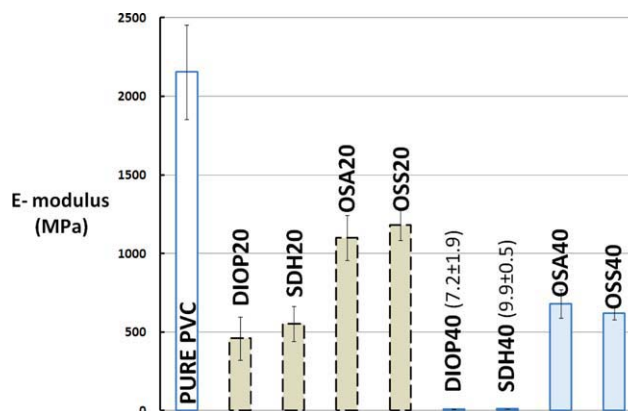| Plasticizer	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	PDI	M_w 10.0% low	M_w 10.0% high
SDH	210	250	280	1,2	90	360
OSS	400	560	820	1,4	190	1440
OSA	260	440	750	1,7	100	1310
OSA 8H	530	1180	2120	2,2	160	3620
OSA D	420	700	1000	1,6	150	1670
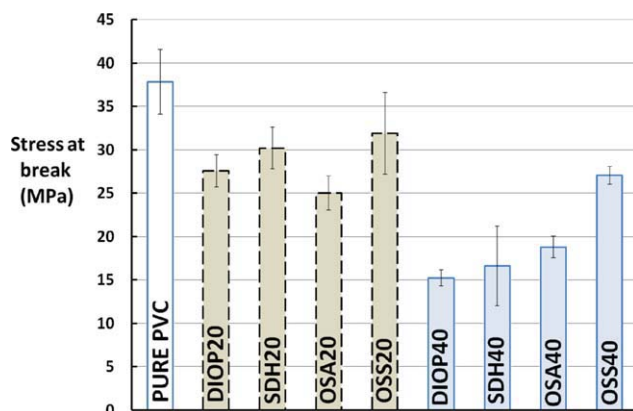
Figure 3 Stress at break for PVC films containing 20 or 40 wt % of the different plasticizers, DIOP, SDH, OSA, and OSS. In the abbreviations the number 20 or 40 indicates the weight percent of plasticizers in the films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

respectively. At 40 wt % the films plasticized with SDH exhibited similar tensile strain at break values compared to the films containing commercial plasticizer DIOP, while the other isosorbide plasticizers had somewhat lower tensile strain values. At 20 wt % all the films plasticized with DIOP and different isosorbide plasticizers exhibited rather similar tensile strain at break values. Of all the studied PVC/plasticizer blends, only SDH40 and DIOP40 films showed elastomeric stress–strain curves, i.e., no yield point was found until break. The films plasticized with 40 wt % of oligomeric plasticizers, OSA and OSS, showed lower tensile strain at break and higher tensile stress at break compared to SDH plasticized films. However, OSS40 films showed both higher stress and elongation at break compared with OSA40 films. They also had lower modulus. Since
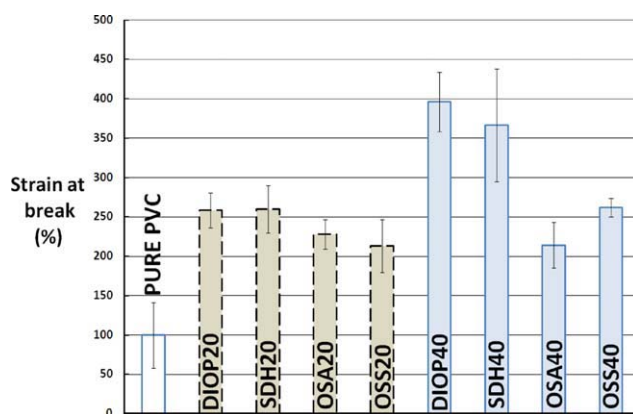
Figure 4 Strain at break for PVC films containing 20 or 40 wt % of the different plasticizers, DIOP, SDH, OSA, and OSS. The number 20 or 40 in the abbreviations indicates the weight percent of plasticizers in the films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5 *E*-modulus for PVC films containing 20 or 40 wt % of the different plasticizers, DIOP, SDH, OSA, and OSS. The number 20 or 40 in the abbreviation indicates the weight percent of plasticizer in the films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the molecular weight of the oligomeric plasticizers, OSS and OSA are rather similar, the more flexible structure of OSS, leading to lower glass transition temperature for the blends is the probable explanation to higher tensile strain at break.

In Table II, the mechanical properties of the films with different OSA plasticizers are compared. At 20 wt % the differences in plasticizer molecular weight had no notable effect on the stress and strain at break or modulus. For the blends with 40 wt % plasticizers a small increase in modulus was observed as the molecular weight increased. A small decrease in modulus was observed for the blend containing OSA-D with methyl ester end groups. However, the molecular weight range studied was rather narrow, and there were not any large effects on mechanical properties. Similar results were also reported by Lindström and Hakkarainen[13] when they studied poly(butylene adipate) based polymeric plasticizers for PVC.

Surface chemistry and miscibility

FTIR has in several studies been used to analyze other PVC/plasticizer systems and their miscibility.[23,24] The carbonyl absorption band from the plasticizer shifts its positions in relation to pure plasticizer. This shift is caused by intermolecular interactions, attributed to the C=O···H—C—Cl dipole–dipole bonds, which are important for the formation of miscible blends and can, thus, be applied when evaluating the miscibility of PVC and ester/polyester blends. All the PVC films plasticized by isosorbide plasticizers and DIOP were analyzed by FTIR, and the shifted values of carbonyl group absorption bands are listed in Table III. In all the blends, the carbonyl group absorption band shifted

TABLE II
Mechanical Properties of PVC Films Containing 20 and 40 wt % of OSA Plasticizers with Different Molecular Weights

Films	Stress at break (MPa)	Strain at break (%)	Modulus (E-modulus) (MPa)
OSA20	25 ± 2	228 ± 19	1100 ± 143
OSA-D20	31 ± 3	227 ± 26	1113 ± 32
OSA-8H20	30 ± 4	227 ± 30	1007 ± 82
OSA40	19 ± 1	214 ± 29	679 ± 89
OSA-D40	21 ± 3	219 ± 31	539 ± 19
OSA-8H 40	25 ± 1	253 ± 8	788 ± 59

to a lower frequency compared to pure plasticizer and the shift was larger with lower amount of plasticizer.

In the OSS/PVC blends the existence of double carbonyl bands was observed (Fig. 6). Because of the similar size of these two carbonyl bands it seems that half of the carbonyl groups in the OSS formed strong secondary bonds to PVC, which caused a larger shift in the carbonyl absorption band. This could be related either to the different stereo structures of the carbonyl groups or to the distance between the carbonyl groups in the suberic acid unit. Since this doublet was not detected in any of the PVC/OSA blends it seems more probable that the distance between the carbonyl groups in the suberic acid only allowed one of the carbonyl groups to form a dipole–dipole bond to the PVC chain. General agreement was also found between the shifted values and the mechanical strain as samples with higher shift of carbonyl group absorption band exhibited larger elongation at break and lower modulus. The surfaces of the blends were also monitored by SEM and by polarized light optical microscopy. The surfaces were shown to be smooth and no crystallites or obvious phase separation was seen. Polarized light optical microscopy did not show any crystalline structures. SEM and polarized light micrographs of OSS20 blend are shown as examples in Figure 7.

Glass transition temperature and miscibility

The glass transition temperatures of plasticized PVC films were determined by DSC. Because of the low

molecular weight of the plasticizers and bulkiness of isosorbide unit, no crystallinity was observed. A single glass transition temperature for each of the studied blends provided proof of miscibility between the isosorbide plasticizers and PVC. The decreasing glass transition temperature for the blends as a function of plasticizers concentration is shown in Figure 8. At the same plasticizer concentration the films plasticized by DIOP and SDH showed a lower glass transition temperature compared to those containing OSA and OSS. OSS blends had lower glass transition temperature compared to OSA blends probably due to the more flexible structure of the plasticizer which generally leads to lower glass transition temperature. A much broader transition temperatures were observed in PVC/OSS and PVC/OSA films, which can be explained by the wider molecular weight distribution or somewhat lower miscibility compared to PVC/SDH blends. The glass transition temperatures for the different blends varying from above room temperature to considerably under room temperature correlated well with the mechanical properties.

Thermal stability of the blends

The thermal stability of PVC films plasticized by 40 wt % isosorbide plasticizers and DIOP were

TABLE III
Shifting of the FTIR Carbonyl Group Absorption Band in the Plasticized Films

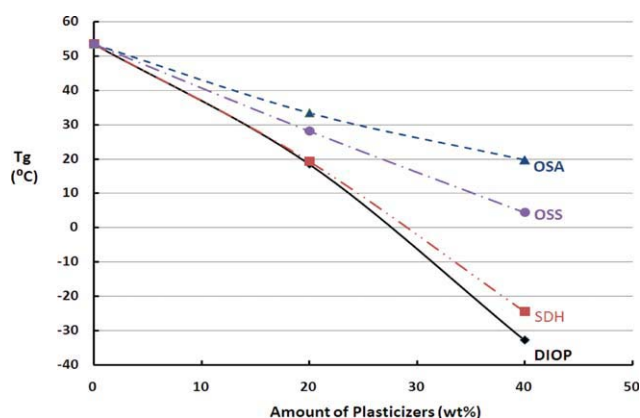| Plasticizer (wt %)	OSA	SDH	OSS	DIOP
20	1732	1732.7	1732.3 1704.8	1718.3
40	1732.3	1733.7	1732.5 1702.5	1720.2
100	1735.6	1740.3	1737.1	1738.6
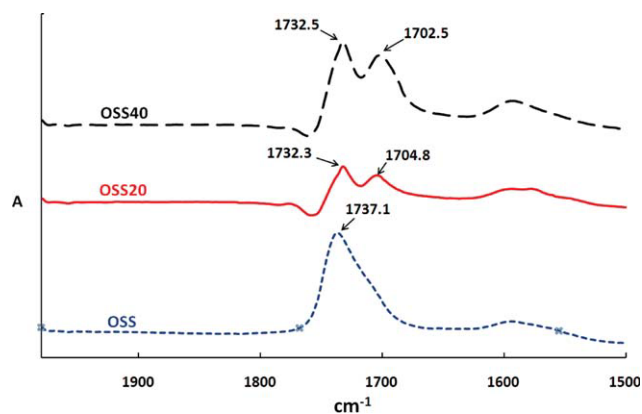
Figure 6 FTIR spectra showing the carbonyl region of pure OSS plasticizer and PVC films plasticized with 20 and 40 wt % OSS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]
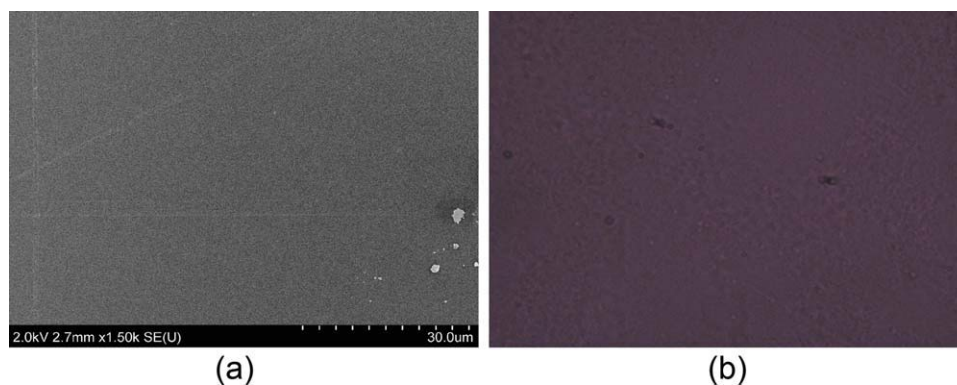
Figure 7 (a) SEM and (b) polarized light micrographs showing the surface of OSS20 blend. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
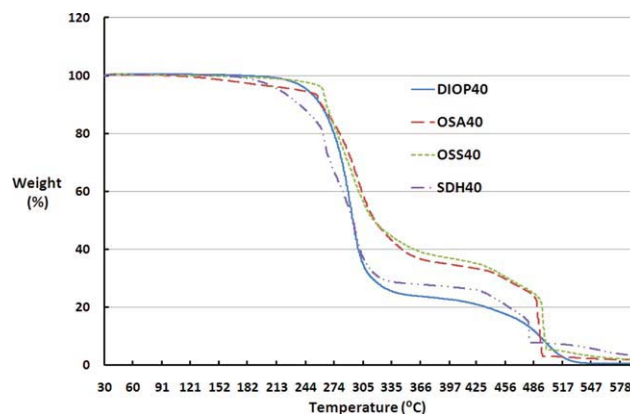
analyzed by TGA and the results are shown in Figure 9. The PVC/SDH blend with alternative monomeric plasticizer, SDH, had lower onset of degradation temperature compared to PVC/DIOP. PVC plasticized with oligomeric plasticizers, OSA and OSS, had higher onset of degradation and, thus, somewhat better thermal stability compared to the films plasticized with monomeric SDH plasticizer, which could mainly be due to the lower volatility of these plasticizers. The shape of the curves and remaining residue after different degradation stages also differed quite markantly between the PVC plasticized with oligomeric plasticizers versus PVC plasticized with DIOP and SDH. PVC/OSA and PVC/OSS exhibited a sharp change at the onset of degradation, after which their weight decreased at slower rate, while the opposite was seen for PVC/DIOP. All the three tested isosorbide plasticizers could have potential as alternative PVC plasticizers. Especially the blends containing SDH had almost identical properties with PVC/DIOP blends.

CONCLUSIONS

OSA, OSS, and SDH were synthesized and blended with PVC. The blends plasticized with SDH showed similar behavior than the blends containing same amount of traditional phthalate plasticizer. The films plasticized by OSA and OSS showed higher glass transition temperature, lower tensile strain at break, and higher tensile stress at break compared to SDH or DIOP plasticized films. Compared to OSA the structure of OSS is more flexible and leads to lower glass transition temperature for the blends, which is also the probable explanation to somewhat higher tensile strain at break. All the prepared blends showed a shift in the FTIR carbonyl group absorption band indicating miscibility through formation of secondary bonds between PVC and the plasticizers. In the OSS/PVC blends, the existence of double carbonyl bands was observed, indicating that only half of the carbonyl groups in OSS formed strong secondary bonds with PVC. Blends containing OSA and OSS plasticizers showed somewhat better

Figure 8 Glass transition temperatures for PVC films containing 0, 20, and 40 wt % of different plasticizers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 9 TGA curves showing the remaining sample weight as a function of temperature for PVC films containing 40 wt % of different plasticizers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

thermal stability compared to the blends containing SDH. All the three isosorbide plasticizers could have potential as alternative PVC plasticizers.

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