Migration resistant glucose esters as bioplasticizers for polylactide

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ABSTRACT: Environmental and sustainability issues have catalyzed efforts to replace traditional polymer additives with biobased alternatives. Glucose pentaacetate (GPA) and sucrose octaacetate (SOA) as model commercial saccharide esters and three synthesized glucose hexanoate esters (GHs) were evaluated as bioplasticizers for polylactide (PLA). For the GHs different reaction times were utilized to reach plasticizers with different number of hexanoate groups to establish how the degree of substitution influences miscibility and migration resistance of the plasticizers. The synthesized GHs, GPA, and SOA all showed good miscibility with PLA. Largest improvements in strain at break were observed for the PLA films containing GH plasticizers. These films also exhibited simultaneous increase in stress at break as compared to plain PLA. The GH plasticizers had low tendency to migrate during aging in water and this migration resistance increased with increasing degree of substitution. The GHs are, thus, promising plasticizer alternatives for bioplastics as they also retain the biodegradable nature of these biobased materials. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41928.

INTRODUCTION

Environmental and sustainability issues have catalyzed efforts to replace traditional polymer additives through utilization of biobased resources. This issue is even more critical in the case of biobased polymers to retain the green nature of the materials. Polylactide (PLA) is among the most interesting degradable biobased materials.[1] In addition to the original biomedical applications, progress in the manufacturing processes has led to economically feasible production of PLA for packaging applications. Plasticization is, however, generally required to overcome the inherent brittleness of PLA.[2] Several plasticizers for polylactide are reported in the literature including cyclic lactides and oligolactic acid, PEG monolaurate,[3–5] citrate esters,[6,7] *bis*(2-ethylhexyl) adipate,[7] and polymeric additives.[8,9] Toughening through reactive extrusions with PEG derivatives has also been demonstrated.[10] Decreased glass transition temperature, T_g, is an indicator of miscibility and efficiency of the plasticizers. In previous literature, the addition of 10–20 wt % of oligolactic acid decreased T_g from 58 to 37°C and 18°C, respectively.[4] PEG monolaurate as PLA plasticizer lowered T_g from 58 to 21°C when 20 wt % plasticizer was added into PLA matrix.[4] Different citrate esters also efficiently increased the chain mobility of PLA and decreased the T_g. Elongation at break is another important indicator of the efficiency of plasticizers. Addition of 20 wt % PEG or PLA oligomer increased the elongation at break from 9 to 142% and 200%, respectively.[4]

Blending 20 wt % of *bis*(2-ethylhexyl) adipate or acetyl tributyl citrate into PLA increased the elongation at break blends from 11 to 78% and 317%, respectively.[7]

The migration of plasticizers from polymer products is a potential problem causing fast deterioration of material properties. In the case of degradable materials the environmental sustainability of the additives and their effect on the degradation rate are additional concerns.[11–13] Chromatographic and mass spectrometric techniques are ideal tools for following the migration of additives and degradation products from polymeric materials under the influence of different simulated, accelerated or real environments.[14,15] Depending on the nature of the plasticizer, it can accelerate or prohibit degradation by influencing material properties such as the degree of crystallinity, glass transition temperature, and hydrophilicity. As an example, lactide and oligolactic acid plasticizers are environmentally degradable, non-toxic additives known to function well as polylactide plasticizers. However, they migrate rather easily in contact with aqueous solutions resulting with time in a stiff material.[16] Linear oligolactic acid also accelerated the hydrolysis of polylactide matrix. In contrary, the addition of hydrophobic citrate plasticizers stabilized polylactide matrix against hydrolysis.[17]

Glucose is a common renewable molecule and a building block for several of the most abundant natural polymers. The developments in biomass utilization and liquefaction processes have
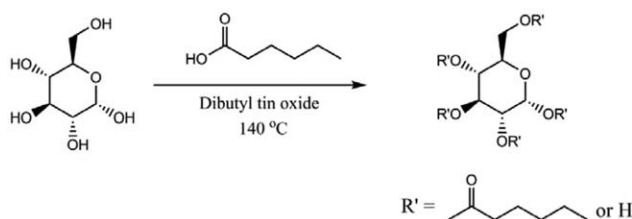
Figure 1. Schematic presentation over the synthesis of glucose hexanoate esters.

made cellulose a promising nonfood resource for large-scale production of valuable green chemicals inclusive glucose.[18–20] It is, thus, becoming possible to decrease the cost of glucose and utilize it in industrial scale without consuming food resources. Buchanan *et al.* first patented carbohydrate esters and polyols ester as plasticizers for cellulose esters, PVC and PLA.[21] The purpose of this study was to develop novel bioplasticizers that do not compromise the green, biodegradable, and sustainable nature of polylactide materials at the same time as they can be produced in large scale from nonedible biomass resources. Hence, glucose-based ester plasticizers were synthesized and evaluated with respect to their miscibility with PLA, plasticization efficiency, and migration resistance.

EXPERIMENTAL

Chemicals
α-D-Glucose (anhydrous, 96%), α-D(+)-glucose pentaacetate (GPA) (99%), D-(+)-sucrose octaacetate (SOA) (98%), ethyl acetate (≥99.9% GC degree), hexanoic acid (HA, 99%), and dibutyl tin oxide (98%) were obtained from Sigma-Aldrich Chemie GmbH. Polylactide (PLA) was from NatureWorks PLA (5200D). Chloroform (HPLC grade) was from Fisher Scientific and sodium carbonate anhydrous and sodium chloride were from Fluka (Sigma-Aldrich).

Synthesis of Glucose Hexanoate Esters
Glucose esters were synthesized according to previously reported procedure.[22] Briefly, 0.1 mol glucose, 0.8 mol HA and 0.6×10^{-3} mol dibutyl tin oxide were heated in round-bottom flask for 9, 12 and 24 h at 140°C under nitrogen. The products were denoted GH9, GH12, and GH24 according to the reaction time. Unreacted HA was neutralized by sodium carbonate. The solution was then extracted with ethyl acetate. Sodium chloride solution was added to improve the phase separation. The ethyl acetate phase containing the glucose esters was collected. The glucose hexanoate esters were separated from ethyl acetate by rotary evaporator and further dried in vacuum oven. The synthesis reaction is schematically presented in Figure 1.

Preparation of Plasticized PLA Films by Solution Casting
PLA films with 10 or 20 wt % of bioplasticizers, B-GH9, B-GH12, B-GH24, B-GPA, or B-SOA, were prepared by solution casting, which is a common way to produce films in laboratory scale. 40 ml chloroform was slowly added into the mixture of plasticizer candidates and PLA at room temperature under stirring. The temperature was then slowly raised to 45°C and the solution was stirred for approximately 1.5 h to completely dissolve PLA. The solution was subsequently poured into a petri dish and dried for several days at room temperature to evaporate the chloroform. The drying process was finalized in vacuum oven at room temperature for 7 days. The thickness of obtained films was 0.15 ± 0.03 mm.

Characterization of the Plasticizers and Their Blends with PLA
The glucose hexanoates were characterized by Bruker Avance III HD 400NMR instrument with BBFO probe, Z-gradient, and automated tuning and matching device (ATM). ^{1}H NMR was measured at 400 MHz and ^{13}C NMR at 100 MHz. The analyses were carried out at room temperature. Mechanical properties of the blends were determined at room temperature by Single Column Table Top Instron 5944. Load cell was 500N and crosshead speed was 50 mm/min. Elongation of the testing specimens was measured automatically by the software from the grip separation. Before the tensile test, samples were cut into strips with width of 5 mm, and a gauge length of 25 mm. The thickness of each sample was measured at several places by digital thickness gage (Mitutoyo micrometer). The average thickness of the films was 0.15 ± 0.03 mm. They were conditioned in the test room with a humidity of 50% for 40 h. At least five specimens from each material were tested. Thermal properties of the films were measured by Mettler Toledo DSC 820 module instrument. Analyses were done under nitrogen atmosphere. The samples were heated from −50 to 200°C with a rate of 10°C/min and held for 2 min at 200°C, thereafter cooled down to −50°C with a rate of −10°C/min and kept constant for 2 min and then increased back to 200°C. Glucose hexanoate esters and water phases after hydrolysis were analysed by ESI-MS in positive mode. The apparatus was ion trap mass spectrometer (ESQUIRE, Bruker Daltonics) with EsquireControl (Bruker Daltonics). The applied voltage for ion source was 4 kv and capillary heater was set to 175°C. Compressed air was used as nebulising gas and damping gas. Syringe pump was set to 5 μl/min. The synthesized GHs were dissolved in water methanol mixture ($V_{water} : V_{methanol} = 2 : 1$) with concentration of 0.001 mg/ml. Degradation solutions were diluted with half volume methanol to obtain the same 2 : 1 ratio.

Hydrolytic Aging
Aging of PLA and 20 wt % plasticizer films was performed in water at 37 and 60°C for 1 day, 1 week, and 3 weeks. Aging was conducted in 20 ml vials containing 10 ml LC–MS grade water. Approximately 40 mg of 1 cm diameter circular film was put in each vial, triplicate samples were prepared and the vials were closed with butyl/polytetrafluoroethylene septa and aluminium lids. After the predetermined aging times, the remaining solid PLA was taken out from hydrolysis medium, dried under vacuum, and weighted. Triplicate samples were taken out for each sample and aging time and the average was calculated. The water solution with migrants were saved and analyzed by ESI-MS.

RESULTS AND DISCUSSION

Three different glucose hexanoate esters with different degrees of substitution were synthesized and evaluated as green plasticizers for PLA. In addition, PLA was also blended with two
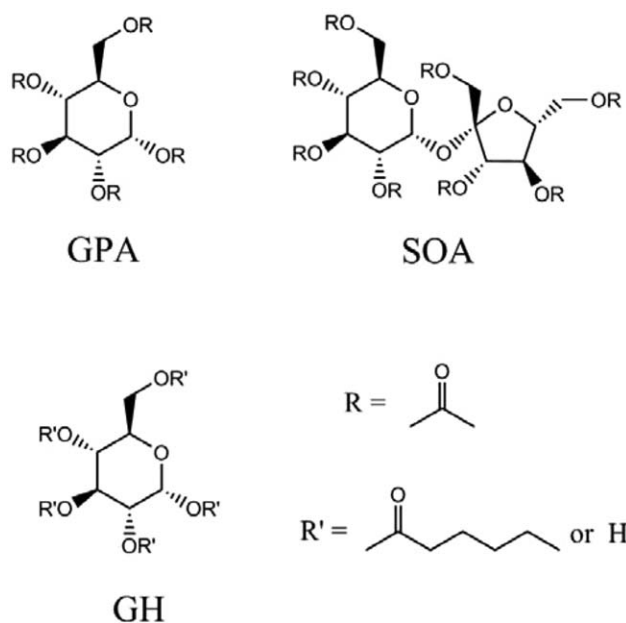
Figure 2. Structures of glucose pentaacetate (GPA), sucrose octaacetate (SOA), and glucose esters (GH).

model saccharide esters, glucose pentaacetate, and sucrose octaacetate. The plasticized PLA films were evaluated with respect to migration resistance, mechanical properties, and miscibility of the new bioplasticizers. The main chemical structures of the commercial bioplasticizers used and the anticipated structures for the synthesized bioplasticizers are presented in Figure 2.

Characterization of the Synthesized Glucose Esters
The successful synthesis of GH9, GH12, and GH24 esters was confirmed by ^{1}H and ^{13}C NMR (Figure 3) and ESI-MS (Figure 4). The NMR analysis showed a mixture of products with different degrees of substitution. Although it is difficult from the obtained complex NMR spectra to identify the individual molecules, the overall integrals over glucose and hexanoic acid originating peaks clearly demonstrate that the degree of substitution, i.e., the average number of hexanoate units per glucose increased with reaction time.

A successful reaction and formation of ester bonds is clearly illustrated by the peak at 173.38 ppm in the ^{13}C NMR spectra in Figure 3(b) originating from a carbonyl carbon in the formed ester bonds. This carbonyl carbon is clearly shifted as compared to the carbonyl carbons of nonreacted hexanoic acid, Figure 3(b). After 9 and 12 h reaction, the carbon peaks originating from glucose are very similar. However, the pattern is somewhat simplified after 24 h of reaction, indicating a less complex product mixture due to higher degree of substitution with respect to the hydroxyl-groups.

For more detailed information of the individual molecular species, ESI-MS analysis was performed on the product mixtures after different reaction times. The glucose hexanoate ester sodium adducts would have $m/z = 301$, 399, 497, 595, or 693 depending on the degree of substitution, i.e., the number of hexanoate units attached. In a similar manner a series of peaks could be observed for glucose dimer hexanoates at $m/z = 757$,

855, 953, and 1051. In addition, the glucose esters can form dimer clusters, consisting for example of two GH_2 molecules and one sodium with $m/z = 775$ or one GH_2 and one GH_3 with one sodium at $m/z = 873$. In the ESI-MS spectra, Figure 4, peaks corresponding to sodium adducts of different glucose esters and clusters of some of the glucose esters were observed. After 9 h of reaction, the two most intense peaks corresponded to GH_3 and GH_4, i.e., glucose substituted with three or four hexanoate units, followed by a peak corresponding to GH_2. When the reaction time was prolonged to 12 h, the most intense peaks still correlated to GH_3 and GH_4. However, the relative amount of GH_4 in relation to GH_3 had increased. In addition a glucose dimer with five hexanoate units was detected indicating a reaction between two glucose units during prolonged reaction time. After 24 h of reaction (GH24), the most intense peak in the mass spectra still corresponds to GH_4. GH_2 had, however, reacted further and was no longer detected. At the same time the relative amount of GH_5 had increased and
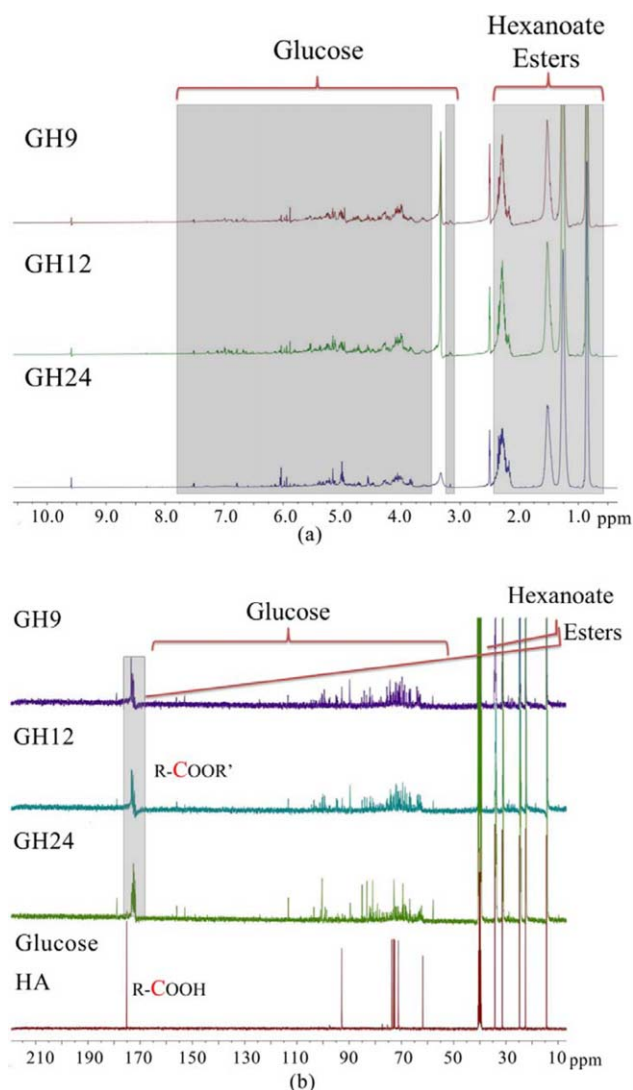

Figure 3. (a) ^{1}H NMR, (b) ^{13}C NMR spectra of GH9, GH12, GH24, and a mixture of glucose and hexanoic acid standards. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
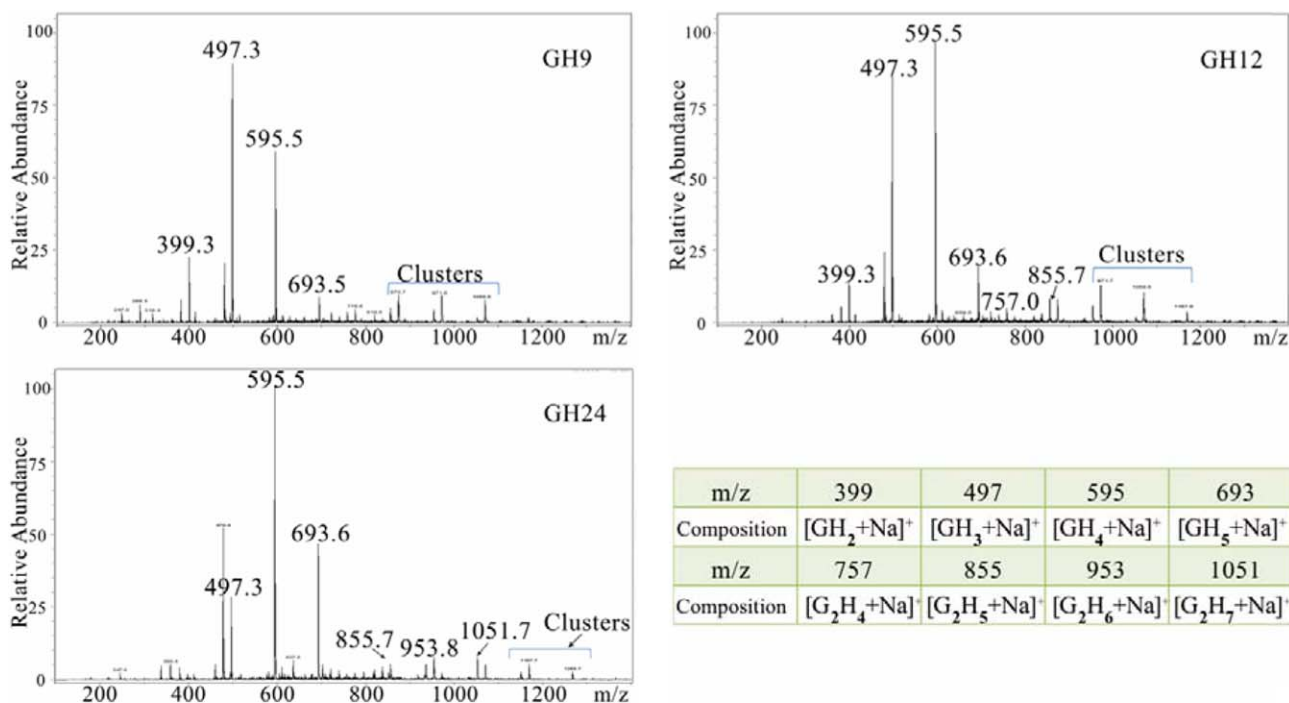
Figure 4. ESI-MS spectra of GH9, GH12, and GH24. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

glucose dimers with higher degree of substitution were detected. In good agreement with NMR results, these results prove that longer reaction time led to higher degree of substitution and formation of glucose oligomers.
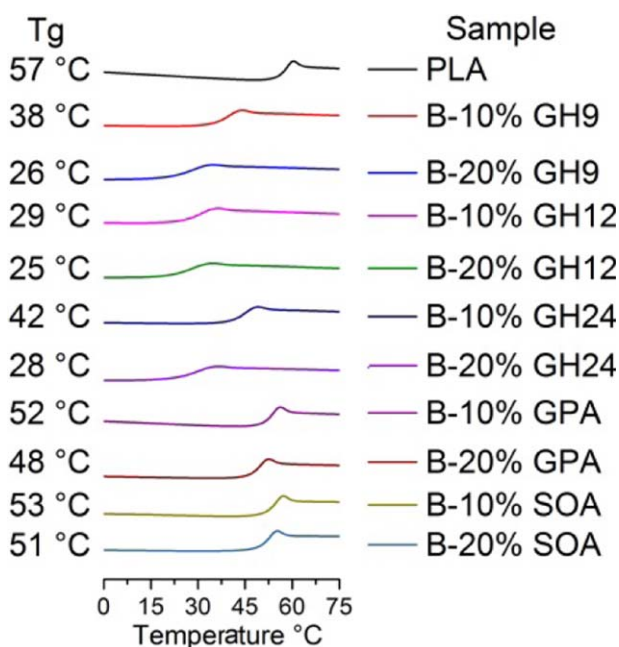

Figure 5. The glass transition temperatures of PLA and PLA/plasticizer blends. Square = 10 wt % blend, circle = 20 wt % blend. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Miscibility Between PLA and Glucose Esters

The glass transition temperatures, T_g, of the prepared films were monitored by DSC to evaluate the miscibility between PLA and the different esters. Single glass transition was observed for all the prepared blends showing that the blends were miscible. The results shown in Figure 5 demonstrate that the T_g for the blend films were clearly lower than the T_g of pure PLA. However, the T_g values were in most cases still slightly above the room temperature. The T_g of all the 20 wt % films with B-GH9, B-GH12, and B-GH24 as well as the T_g of 10 wt % B-GH12 films were close to room temperature, which agrees with the higher tensile strains recorded for the GH blends in comparison with B-GPA and B-SOA blends. Increasing the plasticizer content to 30 wt % could decrease the T_g of the blends to under room temperature providing that antiplasticization effects are avoided and that full miscibility still complies. Samples containing 30 wt % of GHs were therefore prepared, but they were sticky and difficult to handle and were excluded from further studies.

Compared to previous studies with well-known PLA plasticizers, the addition of 20 wt % triethyl 2-acetylcitrate as PLA plasticizer decreased the T_g from 59 to 30°C.[6] *Bis*(2-ethylhexyl) adipate (DOA), acetyl tributyl citrate (ATBC) were also reported as good plasticizers for PLA.[7] Adding 10 wt % of these plasticizers decreased T_g from 62 to 45°C and 44°C, respectively. Larger amount of DOA did not lead to further T_g decrease due to its partial miscibility, while addition of 20 wt % ATBC additionally decreased T_g to 38°C. Our PLA/GH plasticizer blends all showed lower T_g than those reported above for commonly used PLA plasticizers.

The plasticizer structures presented in Figure 2 help us to understand the effect of plasticizer structure on the T_g values.

Table I. Mechanical Properties of the Films

Sample	Amount of plasticizer (wt %)	Tensile strain (%)	Tensile strength (MPa)	E modulus (MPa)
PLA	0	250 ± 18	13 ± 1.0	1690 ± 152
B-GH9	10	380 ± 25	22 ± 2.5	790 ± 104
	20	360 ± 26	19 ± 1.3	630 ± 80
B-GH12	10	340 ± 22	15 ± 1.0	360 ± 45
	20	350 ± 28	23 ± 2.8	880 ± 100
B-GH24	10	340 ± 24	23 ± 1.9	1060 ± 138
	20	370 ± 18	21 ± 0.8	590 ± 108
B-GPA	10	300 ± 26	13 ± 2.3	830 ± 136
	20	310 ± 14	12 ± 0.3	520 ± 66
B-SOA	10	260 ± 20	12 ± 0.8	1360 ± 332
	20	300 ± 28	12 ± 1.1	820 ± 34

Both GPA and SOA have short arms, while GH plasticizers have longer alkane arms. These longer arms may provide more free volume between the PLA chains leading to somewhat lower T_g values. Dimeric structure of SOA leads to somewhat bulkier molecules, which is the probable reason for higher T_g compared to GPA blends. In similar manner GH24 contains more dimeric structures in comparison to GH12 and GH9, which might explain the slightly higher T_g values.

Mechanical Properties of Glucose Ester Plasticized PLA
All the saccharide esters, including the model esters increased the tensile strain of the films in comparison with tensile strain of pure PLA, Table I. The largest improvement was obtained for B-GH9, followed by B-GH12 and B-GH24. Slightly more moderate increases were observed for B-GPA and B-SOA plasticized with model esters. Increasing the plasticizer concentration from 10 to 20 wt % had only a marginal effect and the further improvements in tensile strain were small.

Table I also presents the tensile strength for all the prepared films. In B-GH9, B-GH12, and B-GH24 materials a simultaneous increase of both tensile strain and tensile strength was observed. Tensile strength of B-GPA and B-SOA remained very similar to that of pure PLA. The reason for it was that compatibility of GPA/SOA in PLA matrix was not as good as it of GHs. GPA and SOA can increase the PLA chain mobility but, for these acetates, the compatibility in PLA matrix was not so good due to their short alkane arms. The tensile properties of B-GPA or B-SOA remained very similar to those of pure PLA. As expected from a good plasticizer, the addition of saccharide esters significantly increased the tensile strain of the films. As shown in Table I, this decrease was generally higher when the plasticizer concentration was increased from 10 to 20 wt %.

Mass Loss During Hydrolytic Aging
The PLA films with 20 wt % plasticizer were aged in water at 37 and 60°C for 1 day, 1 week, and 3 weeks. Figure 6(a,b) shows the mass loss of the films during aging at 37 and 60°C, respectively. The mass loss of all the samples increased with time and it was higher after aging at 60°C as compared to aging at 37°C. There were no large differences between the different samples, but a few

interesting trends could be observed. After aging at 37°C, the mass loss of the glucose ester plasticized films was very close to the mass loss of pure PLA, generally within ±1%, indicating that no significant plasticizer migration took place. After 3 weeks of hydrolytic aging the differences started to be clearer. Interestingly the mass loss of B-GH12 and B-GH24 was even lower than the mass loss of pure PLA illustrating the very good migration resistance of these plasticizers. The mass loss of B-GH9, B-GPA, and B-SOA was slightly higher than the mass loss of pure PLA. This higher mass loss is deduced to the migration of GH9, GPA, and SOA from the blends, which is supported by the ESI-MS analysis of the migrants presented below.

After aging at 60°C, the mass loss of plasticized films was generally slightly higher than the mass loss of pure PLA films. The B-GH24 blends, however, still exhibited lower mass loss than plain PLA films. After 3 weeks at 60°C the mass loss of B-GH24, 43%, was approximately 10 wt % lower than the mass loss of plain PLA which was 53%. GH24 plasticizer was, thus, not only migration resistant, it also retarded the PLA hydrolysis. Generally, it can be concluded that longer synthesis reaction time and higher degree of substitutions lead to more migration resistant GH plasticizers, which could be connected to improved miscibility and/or lower water solubility. This is in agreement with our previous studies showing that hydrophobic PLA plasticizers are more resistant to migration and that they also retard the hydrolysis rate of PLA, while the hydrophilic plasticizers migrate rapidly and accelerate the hydrolysis of PLA matrix.[16,17]

Migration of Degradation Products and Plasticizers During Hydrolytic Aging
Migration of water-soluble low molar mass compounds from the materials during aging in water was studied by ESI-MS. The most intense MS signal of lactic acid oligomers usually appear as sodium adducts at $m/z = 23 + 72 \times n + 18$, where 72 is the mass of lactic acid repeating unit and 18 is the mass of end groups.[23] According to Figure 7 after 1 day of aging in water at 60°C, no detectable amounts of lactic acid oligomers were observed in any of the samples. Some GH_2 and/or GH_3 had migrated from B-GH9 and B-GH12 and a trace of GH_2 could be detected after aging of B-GH24 films. This amount was,
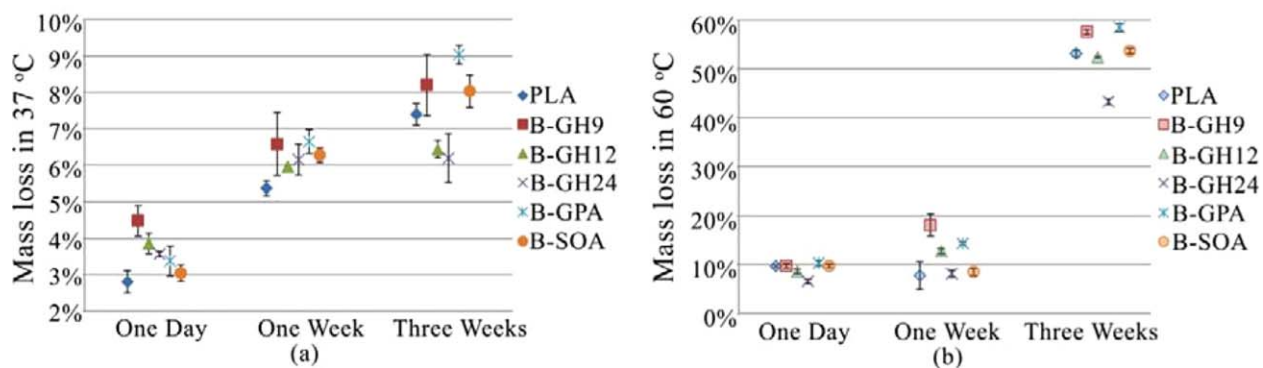
Figure 6. Mass loss for the PLA films after aging in water at (a) 37°C and (b) 60°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
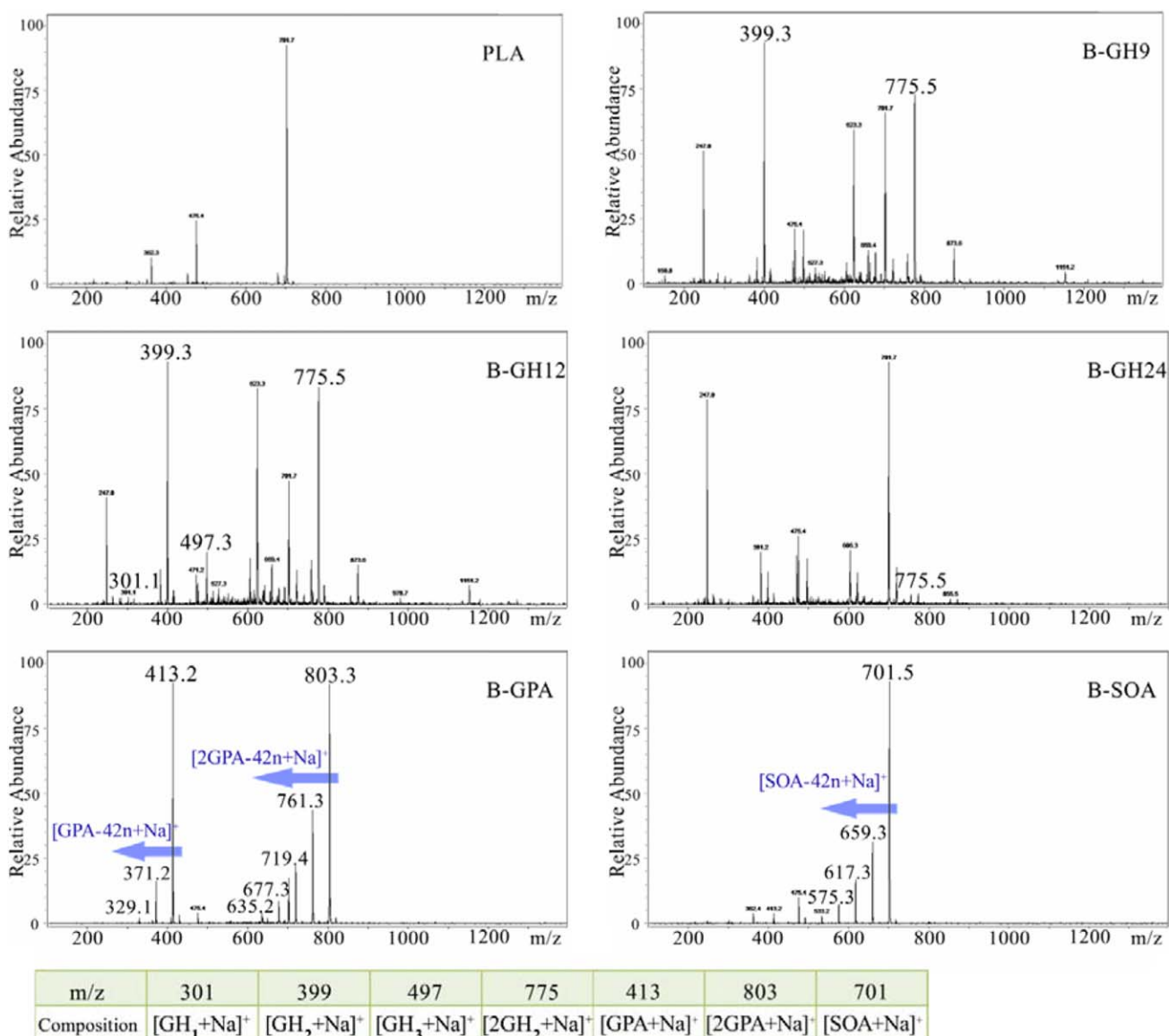

m/z	301	399	497	775	413	803	701
Composition	$[GH_1+Na]^+$	$[GH_2+Na]^+$	$[GH_3+Na]^+$	$[2GH_2+Na]^+$	$[GPA+Na]^+$	$[2GPA+Na]^+$	$[SOA+Na]^+$

Figure 7. ESI-MS spectra showing the compounds that migrated from the different films during 1 day of aging at 60°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
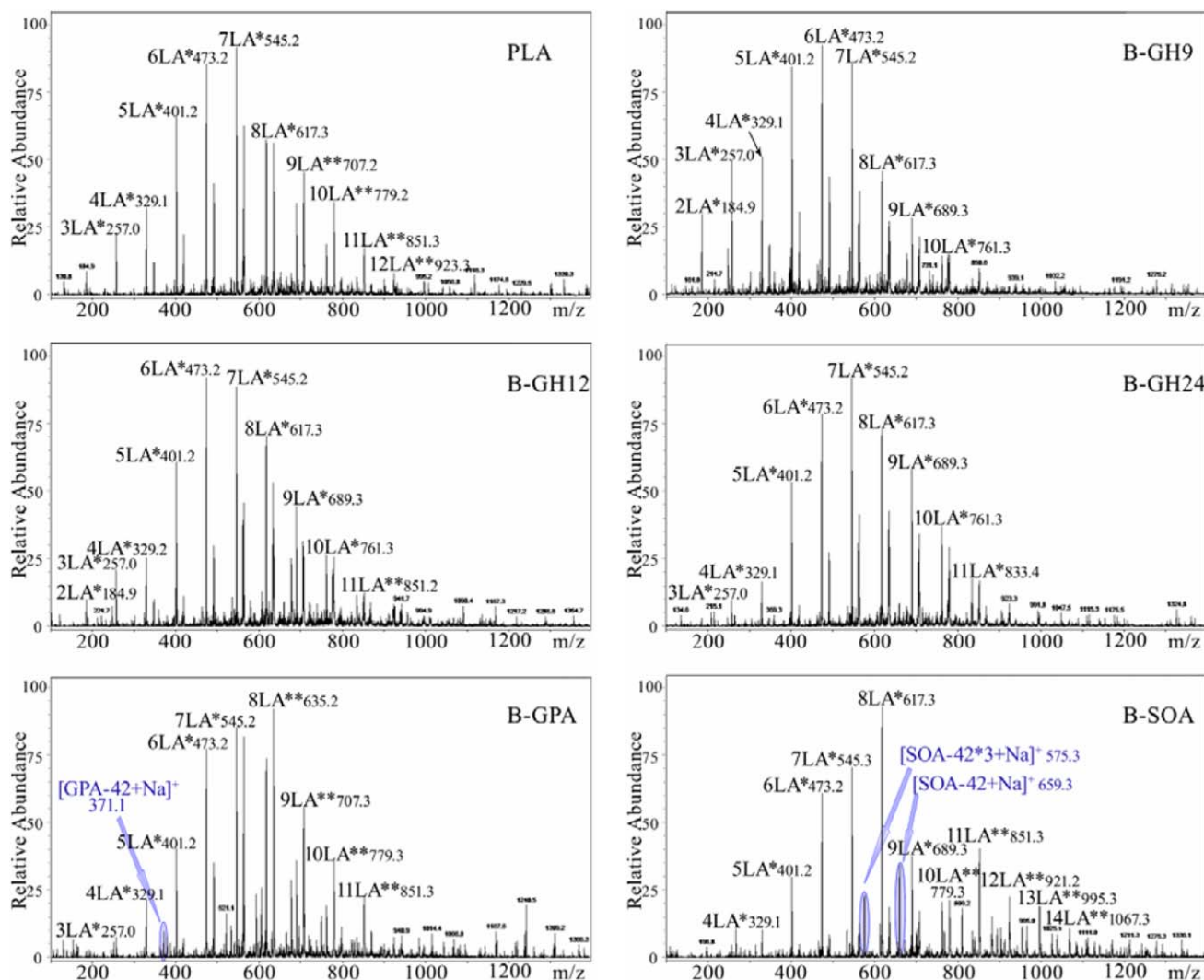
Figure 8. ESI-MS spectra showing the compounds that migrated from the different films during 3 weeks of aging at 60°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

however, significantly smaller as compared to the migration from B-GH9 and B-GH12 films, which is in agreement with mass loss measurements and the original amount of GH_2 in the different blends (see Figure 6). Based on the relative intensity of the ESI-MS peaks, the migration of GPA to the aging water took place at significantly higher rate as compared to the migrations of GH plasticizers, which can be coupled to lower miscibility and higher water-solubility of GPA. After 1 day of hydrolysis strong peaks for GPA sodium adduct at $m/z = 413$ and sodium complex of two GPA molecules at $m/z = 803$ were detected. Peaks corresponding to hydrolyzed GPA formed through loss of one or two acetate groups were also detected at $m/z = 371$ and 329. Hydrolysis products of the dimer complex were detected at $m/z = 761, 719, 677,$ and 635. SOA and its hydrolysis products were also detected as sodium adducts already after 1 day of aging in water at 60°C. SOA at $m/z = 701$ and its hydrolysis products through loss of one or several acetate groups at $m/z = 659, 617, 575,$ and 533 were detected.

After 3 weeks of degradation in water at 60°C, lactic acid oligomers had been formed due to hydrolysis of PLA matrix

and they were detected in all the aging solutions (Figure 8). In fact they were the dominating migrants and in comparison only small traces of peaks corresponding to the plasticizers were detected giving further indication of the good migration resistance of the GH plasticizers. GHs, especially at higher degrees of substitution, are more hydrophobic than GPA and SOA, which increases the migration resistance compared to GPA and SOA. In a similar manner the migration resistance also increases when going from GH9 to GH24. Furthermore, the acetate groups are more easily hydrolyzed due to the more hydrophilic nature and less stereo hindrance around the ester groups. This also further supports the fact that mass losses for the plasticized films were similar or even smaller than the mass losses of plain PLA.

CONCLUSIONS

Glucose hexanoate esters with different degrees of substitution, i.e., number of hexanoate units, were synthesized and demonstrated to be promising bioplasticizers for PLA. The addition of

glucose esters decreased the glass transitions temperature and improved the elongation of PLA films in comparison with plain PLA and PLA plasticized with model glucose and sucrose acetates. In addition the migration resistance of the glucose hexanoate esters was superior in comparison with the model saccharide acetates. The migration resistance increased with increasing degree of substitution.

ACKNOWLEDGMENTS

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