

Liquefied biomass derived plasticizer for polylactide

Edwin Azwar, Bo Yin and Minna Hakkarainen*

Abstract

BACKGROUND: The valorization of renewable agro-industrial residues and their further utilization for production of polymers and polymer additives is a highly attractive alternative for replacement of oil-based materials.

RESULTS: Liquefied wood flour and rice bran derived esters were synthesized and evaluated as novel green plasticizers for polylactide (PLA). The liquefied wood flour ester (PWF) showed good miscibility with PLA and good plasticization efficiency as shown by differential scanning calorimetry (DSC) and tensile testing. Tensile strain at break increased from a few percent for pure PLA to over 100 and 300% for the materials containing 10 and 30 wt-% of PWF. The addition of PWF accelerated the hydrolysis rate of PLA as shown by faster weight loss during aging in water and faster formation of water-soluble lactic acid oligomers, which was shown by electrospray ionization mass spectrometry (ESI-MS) analysis of the migrants. The liquefied rice bran based product (PRB) was not miscible with PLA and it did not improve the elongation at break of PLA. Rice bran is generally rich in arabinoxylans with only secondary less reactive alcohol groups. The larger number of un-reacted hydroxyl-groups in PRB was confirmed by Fourier transform infrared (FTIR) spectroscopy and could explain the immiscibility with PLA.

CONCLUSIONS: The results demonstrate that the synthesized liquefied wood flour derived plasticizer could have great potential as a biobased polylactide plasticizer.

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Keywords: polylactide; biomass; green chemistry; plasticizer; wood; agro-waste; valorization

INTRODUCTION

The production of polymeric materials from non-edible biomass is one of the challenges facing our society.¹ Polylactide (PLA) is one of the most promising renewable resource synthetic polymers. PLA has generally good modulus and tensile strength but it is inherently brittle, which limits the application range. A lot of research has been conducted to toughen PLA through different approaches.² Blending of PLA with plasticizers such as citrate esters³ or with biodegradable low molecular weight polyesters⁴ and polyethers⁵ are some of the approaches tried for improving the flexibility and toughness of PLA. Similar polymeric plasticizers have also been evaluated as alternative plasticizers for PVC.⁶ Any material modification including addition of plasticizers can either accelerate or retard the hydrolytic degradation rate of PLA.⁷ In previous studies it was shown that hydrophobic plasticizers can reduce the water absorption capacity of PLA, which will subsequently protect PLA chains against hydrolysis.⁸ The use of more hydrophilic plasticizers, such as linear lactic acid oligomers, on the other hand, increased the water uptake and accelerated the hydrolysis of polyester chains.⁹ The water-solubility of the plasticizers can also lead to rapid leaching of plasticizers from the material.

Biofibres have been utilized in numerous studies for preparation of degradable PLA biocomposites.^{10–12} Biobased waste products like wood flour,¹³ cellulose,¹⁴ corn bran¹⁵ and waste paper¹⁶ are examples of products that can also be liquefied to low molecular weight polyols for further utilization and synthesis of polymeric materials or polymer additives. Previously these polyols were used

as raw materials for the synthesis of polyurethanes,^{17,18} phenolic and epoxy-resins^{19,20} and polyesters.²¹ We previously designed isosorbide ester based renewable plasticizers²² and also utilized macromolecular engineering to improve the plasticization efficiency of poly(butylene adipate) plasticizers.^{23,24} Our hypothesis was that esters synthesized from liquefied biomass derived polyol mixtures could also function as environmentally friendly plasticizers. The purpose of our study was, thus, to design cheap renewable additives from forest or agricultural waste products and to evaluate these compounds as new green plasticizers for PLA.

MATERIALS AND METHODS

Materials and chemicals

Polylactide used was NatureWorks PLA (5200D). Glycerol and diethylene glycol ($\geq 98\%$) were obtained from VWR (Stockholm, Sweden), hexanoic acid (HA) (99%), p-toluenesulphonic acid ($\geq 98.7\%$), sucrose octaacetate ($\geq 97\%$) and dibutyl tin oxide (98%) were purchased from Sigma-Aldrich Chemie GmbH (Steinheim, Germany). 1,4-dioxane, methanol (HPLC grade), and chloroform (HPLC grade) were obtained from Fisher Scientific (UK Limited)

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and methanol (LC-MS grade) from Fluka. Rice bran and wood flour from hardwood were bought as agricultural waste from local farmers in Indonesia.

Liquefaction of wood flour and rice bran

60 g glycerol, 15 g diethylene glycol, and 2.3 g p-toluenesulphonic acid were placed into a three necked glass reaction vessel and heated with stirring. 12.5 g wood powder or rice bran powder was added gradually when the temperature reached 160 °C; after this the temperature was raised to 180 °C and liquefaction was carried out for 120 min. Liquefied products inside the reaction vessel were diluted with dioxane/water solution (4:1 v/v) after the reaction was finished and cooled down. The diluted sample was then filtered using a pre-weighed Whatman filter paper. The residue on the filter paper was dried in an oven at 120 °C until constant weight to calculate the liquefaction efficiency.

Esterification of liquefied wood and liquefied rice bran mixtures

To synthesize plasticizers from liquefied wood flour (PWF) and liquefied rice bran (PRB), the liquefied product mixtures including the liquefaction alcohols were added into a round-bottomed reaction vessel with allihn condenser together with an excess of hexanoic acid and dibutyl tin (IV) oxide as catalyst. The vessel was heated to 150 °C in a silicone oil bath for 2 h. After cooling, the condenser was changed to a distillation system and the temperature was raised to 180 °C under nitrogen. The reaction was continued for 7 h. The system was cooled down to room temperature and products were dissolved in methanol and precipitated by water in a separatory funnel. The un-reacted monomers (e.g. hexanoic acid) were washed away during this step. The precipitated products were collected for further evaluated as plasticizers.

Preparation of plasticized polylactide films

PLA films with 10 wt-% plasticizer were prepared by weighing 4.5 g of PLA and 0.5 g of PWF or PRB. Films with 30 wt-% plasticizer were prepared by blending 3.5 g of PLA and 1.5 g of PWF or PRB. In addition a film containing 30 wt-% model sucrose octaacetate was prepared. PLA together with the plasticizers were dissolved in 75 mL chloroform at 45 °C for 1 h. The solutions were cast on petri dishes and allowed to air-dry at room temperature overnight. Solvents were removed in a vacuum oven for 7 days at room temperature. The thickness of the resulting films was approximately 160 μm.

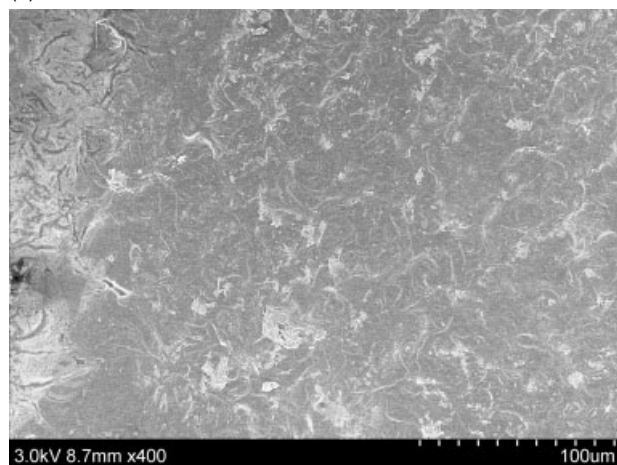
Hydrolysis of plasticized films

PLA films were hydrolytically aged at two different temperatures for four different hydrolysis times. For each time and temperature triplicate samples were prepared of each material. The hydrolysis temperatures were 37 °C and 60 °C and the hydrolysis times were 7, 28, 56 and 84 days. For each sample approximately 15 mg of PLA film was put into 5 mL of LC-MS water. After each hydrolysis time, the remaining PLA film was taken out from the water, wiped with Kleenex and weighed for the wet weight. The films were then dried in a vacuum oven for 1 week and weighed again to obtain the dry weight after hydrolysis. The wet weights were used to

Table 1. Glass transition temperatures of PLA and PLA/ester blends

	T_{g1} (°C)	T_{g2} (°C)
PLA	44	55
PLAPW10	25	27
PLAPWF30	9	12
PLAPRB10	47	50
PLAPRB30	47	49

(a)



(b)

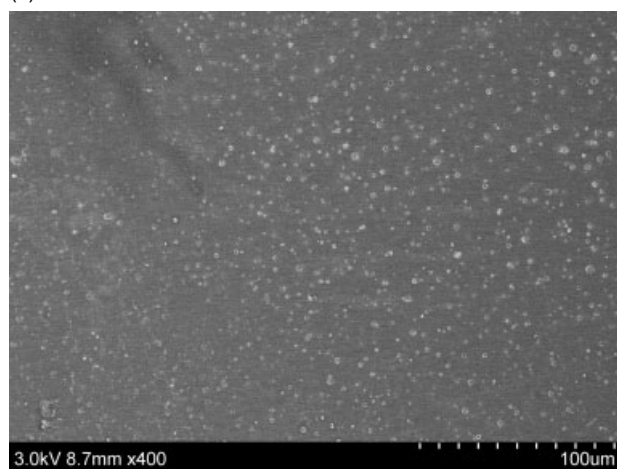


Figure 1. SEM micrographs showing the surface of (a) PLAPWF30 and (b) PLAPRB30.

calculate water absorption and dry weights to calculate mass loss.

$$\text{Water absorption} = \frac{[(\text{wet weight} - \text{dry weight}) / \text{dry weight}] \times 100\%}{}$$

$$\text{Mass loss} = \frac{[(\text{original weight} - \text{dry weight}) / \text{original weight}] \times 100\%}{}$$

Scanning electron microscopy (SEM)

SEM analyses were made using a Hitachi S-4800 ultra-high resolution FE-SEM. Film pieces were mounted on metal studs and

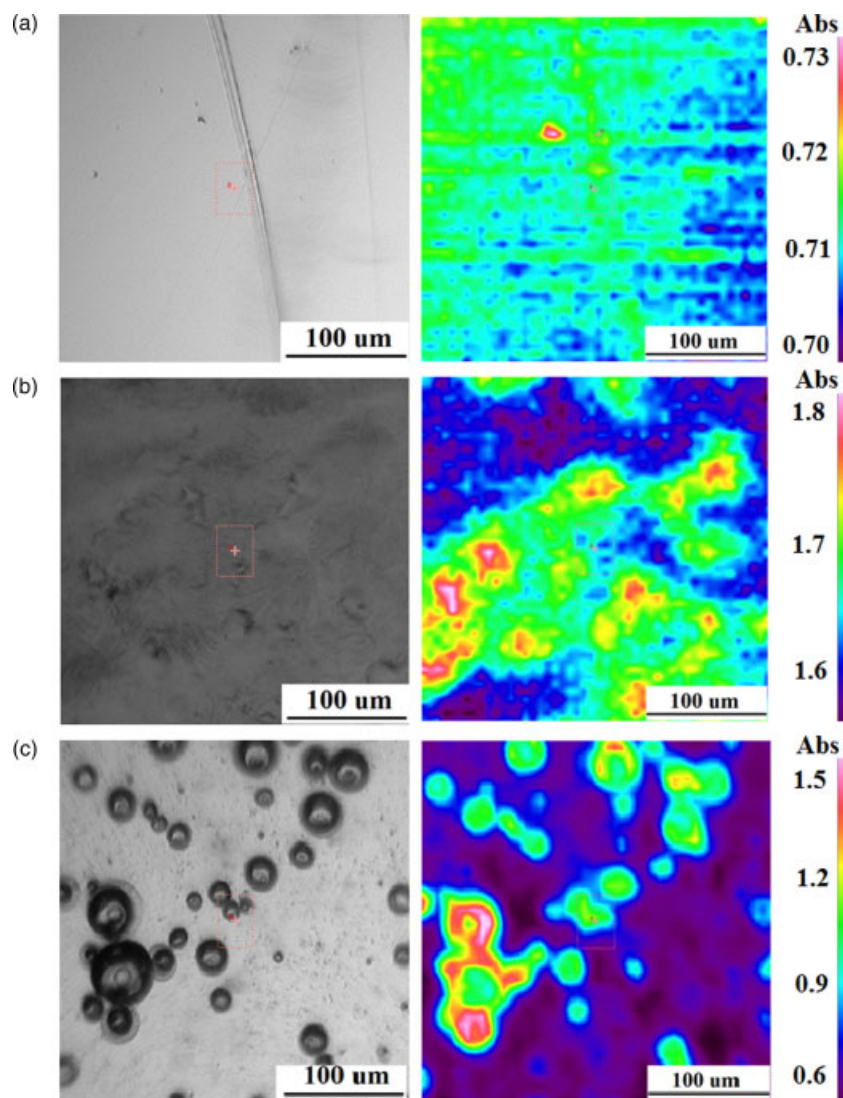


Figure 2. Optical microscopy and FTIR imaging of (a) PLA, (b) PLAPWF30 and (c) PLAPRB30.

sputter-coated with gold–palladium. All samples were examined using an accelerating voltage of 3.0 kV.

Mechanical properties

Mechanical properties were obtained using an Instron Universal testing machine (Model 5566) equipped with pneumatic clamps. The tests were performed with a 500 N load cell with cross-head speed 4 mm min⁻¹. The software program was Bluehill. Before testing, samples were conditioned at 50% relative humidity and 23 °C. Five specimens with rectangular shape (80 × 5 mm) were prepared from each sample using an EP 04/80 × 5 mm specimen cutter (Elastocon AB, Sweden). The sample thickness was measured by digital thickness gauge.

Fourier transform infrared spectroscopy (FTIR)

FTIR spectra were monitored by Perkin Elmer Spectrum 2000 in the range 4000–500 cm⁻¹. The FTIR was equipped with a single reflection attenuated total reflectance crystal accessory (golden gate). FT-IR spectra and single-peak absorbance images of PLA, PLAPWF30 and PLAPRB30 films were also recorded using a Perkin-Elmer Spotlight 400 system equipped with optical microscope

(Bucks, UK). Transmission mode was applied to obtain the image and spectra.

Size exclusion chromatography (SEC)

The molecular weights of the liquefied products were determined by SEC Viscotek TDA model 301 triple detector array SEC apparatus (viscosimeter, refractive index detector, and light scattering detector) equipped with two GMHHR-M columns with TSK-gel, a Viscotek VE 5200 GPC autosampler, a Viscotek VE 1121 GPC solvent pump, a Viscotek VE 5710 degasser, all from Viscotek Corp. Tetrahydrofuran (THF) was used as mobile phase at 1.0 mL min⁻¹. Polystyrene standards were used for universal calibration. Flow rate fluctuations were corrected by toluene as an internal standard. Columns and detectors were kept at 35 °C.

Differential scanning calorimetry (DSC)

A Mettler-Toledo DSC 820 was used to perform the DSC analysis. Around 5 mg of each sample was placed into standard 40 μL aluminum cups. The temperature was increased at 10 °C min⁻¹ from -20 °C to 200 °C and then decreased to -20 °C at the same

rate. Finally, the samples were heated a second time from -20°C to 200°C at a rate of $10^{\circ}\text{C min}^{-1}$. The whole temperature program was performed under nitrogen gas flow of 50 mL min^{-1} .

Electrospray ionization-mass spectrometry (ESI-MS)

A Finnigan LCQ ion trap mass spectrometer (Finnigan, San Jose, CA, USA) was used to analyze the water-soluble migrants from the samples. The water fractions were diluted with methanol (water/methanol = 2:1 v/v). After filtration the samples were infused by the instrument syringe at a constant rate $5\ \mu\text{L min}^{-1}$ and the analysis was performed in positive ion mode. The LCQ ion source was operated at 5 kV and capillary temperature was 175°C .

RESULTS AND DISCUSSION

Wood flour and rice bran were liquefied by acid-catalyzed reaction and the resulting polyol mixtures were reacted with hexanoic acid to synthesize green plasticizer candidates. The liquefaction process was 84% efficient in the case of the wood flour, while only 42% of rice bran was liquefied. This was also reflected by the molecular weight of the liquefied products, as the number average molecular weights of liquefied wood flour and rice bran were 270 g mol^{-1} and 1350 g mol^{-1} , respectively. The main components of wood flour and rice bran are different polysaccharides, which can be liquefied to low molecular polyols. The molecular weight of the liquefied products indicated that wood was mainly liquefied to monosaccharides and disaccharides, while liquefied rice bran was liquefied to oligosaccharides. During the liquefaction reaction liquefaction solvents can also react with ether bonds of the polysaccharides and form monosaccharide and oligosaccharide ethers containing one glycerol or diethylene glycol unit.²⁵ A broad absorption band around 3300 cm^{-1} was seen in the FTIR spectra of original wood flour and rice bran powder and this band further increased in intensity after liquefaction. The formation of a strong carbonyl absorption band at 1730 cm^{-1} after the esterification reaction indicated successful reaction of the polyols with hexanoic acid. The synthesized esters were blended with PLA at 10 and 30 wt-% concentrations to evaluate the plasticization efficiency and miscibility with PLA.

Thermal properties and miscibility of the plasticizers

The differential scanning calorimetry analysis of the prepared blends indicated good miscibility for the liquefied wood flour based esters (PLAPWF) (Table 1). The addition of PWF esters resulted in single concentration dependent glass transition temperatures that were clearly below the glass transition temperature of pure PLA. The addition of 10 wt-% plasticizer reduced the glass transition temperature to approximately room temperature, while the blend containing 30 wt-% plasticizer had a glass transition temperature clearly below room temperature. This was also reflected by the mechanical properties and especially the tensile strain at break values. The liquefied rice bran based esters (PLAPRB) did not significantly lower the glass transition temperature of PLA and did not form miscible blends with PLA. A trace of a melting point was detected for PLAPWF materials indicating after integration less than 1% crystallinity. The films were, thus, practically 100% amorphous and no melting points or degrees of crystallinity are therefore given.

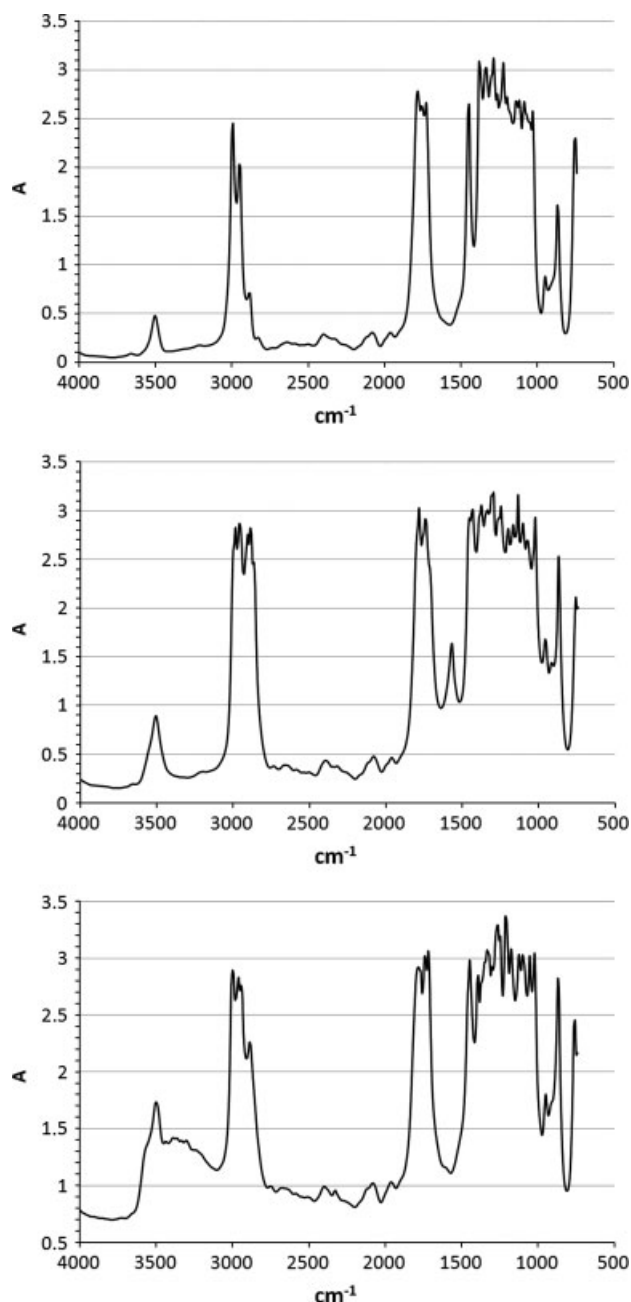


Figure 3. FTIR spectra of PLA (top), PLAPWF30 (middle) and PLAPRB30 (bottom).

Surface analysis

SEM images of the surfaces supported the results from thermal analysis. Figure 1(a) indicates rather even distribution of the liquefied wood flour based plasticizers in the PLA matrix. However, clear phase separation was observed in the case of PLAPRB blends, where the liquefied rice bran based plasticizers appeared as small spheres in the PLA matrix (Fig. 1(b)). FTIR imaging was utilized as an additional tool to evaluate the homogeneity and distribution of carbonyl groups in the films. Figure 2(a) shows optical microscopy and FTIR imaging of plain PLA showing a rather homogeneous material with homogeneous distribution of carbonyl groups. Figure 2(b) illustrates the optical microscopy and FTIR image of PLAPWF30 with wood flour derived plasticizer. The

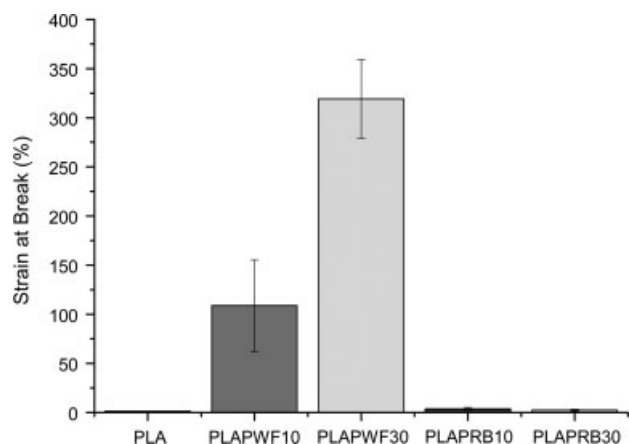


Figure 4. Tensile strain at break for PLA with 10 or 30 wt-% of liquefied wood flour and rice bran based esters.

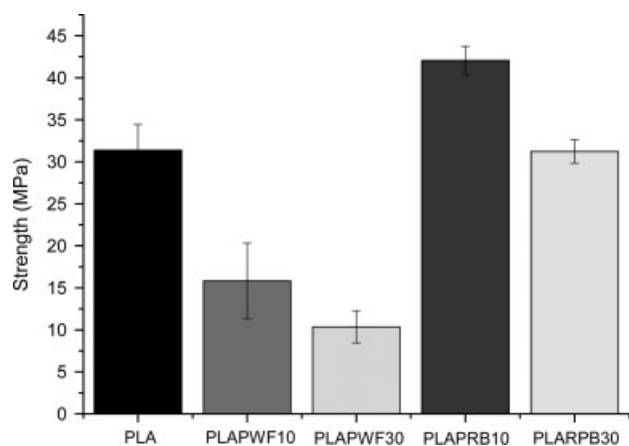


Figure 5. Tensile strength at break for PLA with 10 or 30 wt-% of liquefied wood flour and rice bran based esters.

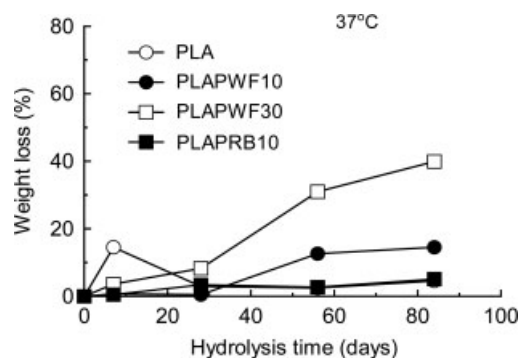


Figure 6. Weight losses for the different PLAs as a function of hydrolysis time at 37°C.

images agree well with the previous results and also with the SEM image in Fig. 1(a) showing rather homogeneous film and relatively homogeneous distribution of the plasticizer. A clear difference is observed in Fig. 2(c) showing the optical microscopy and FTIR images of PLAPRB30. Here clear phase separation between PLA and liquefied rice bran product is seen in the optical microscopy picture and this is further supported by the FTIR imaging showing large variations in the intensity of the carbonyl absorbance band

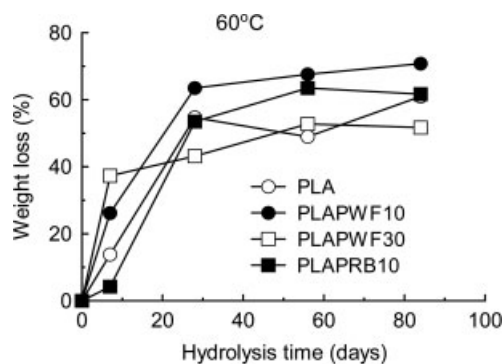


Figure 7. Weight losses for the different PLAs as a function of hydrolysis time at 60°C.

at different parts of the films. These results are in good agreement with the SEM image shown in Fig. 1(b).

Figure 3 illustrates the corresponding FTIR spectra of PLA, PLAPWF30 and PLAPRB30. A comparison of the three spectra shows clear differences in the hydroxyl absorbance area around 3000 cm^{-1} . In all three spectra a relatively sharp band originating from hydroxyl groups in PLA is seen. In the case of PLAPRB30 an additional broad hydroxyl absorbance band is observed indicating a large number of un-reacted hydroxyl groups in the liquefied rice bran product. Rice bran is generally rich in arabinoxylans with only secondary less reactive alcohol groups. The lower ester content and remaining hydroxyl groups leading to more hydrophilic product could be the main reason for the immiscibility of rice bran based product with PLA. In addition the different composition (e.g. proteins and fats in rice bran), lower liquefactions efficiency and higher molecular weight could contribute to the different behavior.

Mechanical properties

The effect of PWF and PRB esters on the mechanical properties of PLA was evaluated by tensile testing. Figure 4 presents the tensile strain at break for PLA, PLAPWF10, PLAPWF30, PLAPRB10 and PLAPRB30. In accordance with DSC results the addition of PWF significantly improved the tensile strain at break of PLA. This was even more marked after addition of 30 wt-% PWF, which resulted in materials with glass transition temperature below room temperature. Tensile strain at break increased from a few percent for pure PLA to over 100 and 300% for PLAPWF10 and PLAPWF30, respectively. The addition of PRB did not improve the tensile strain at break compared with that of pure PLA. Regarding correlation the tensile strength at break for PLAPWF10 and PLAPWF30 were only 50 and 30% of the tensile strength at break for pure PLA, respectively (Fig. 5). PLAPRB30 had almost the same tensile strength at break as pure PLA, while the tensile strength at break for PLAPRB10 was somewhat higher than that of PLA. The tensile strain at break of the film containing 30 wt-% model sucrose octaacetate was 550%. The plasticization efficiency of the pure model disaccharide ester was, thus, even higher than the plasticization efficiency of the mixed PWF ester showing the potential of saccharide esters as PLA plasticizers.

Hydrolytic aging of the materials

The influence of the new plasticizers on the hydrolytic degradation rate was evaluated by following the weight loss and migration of

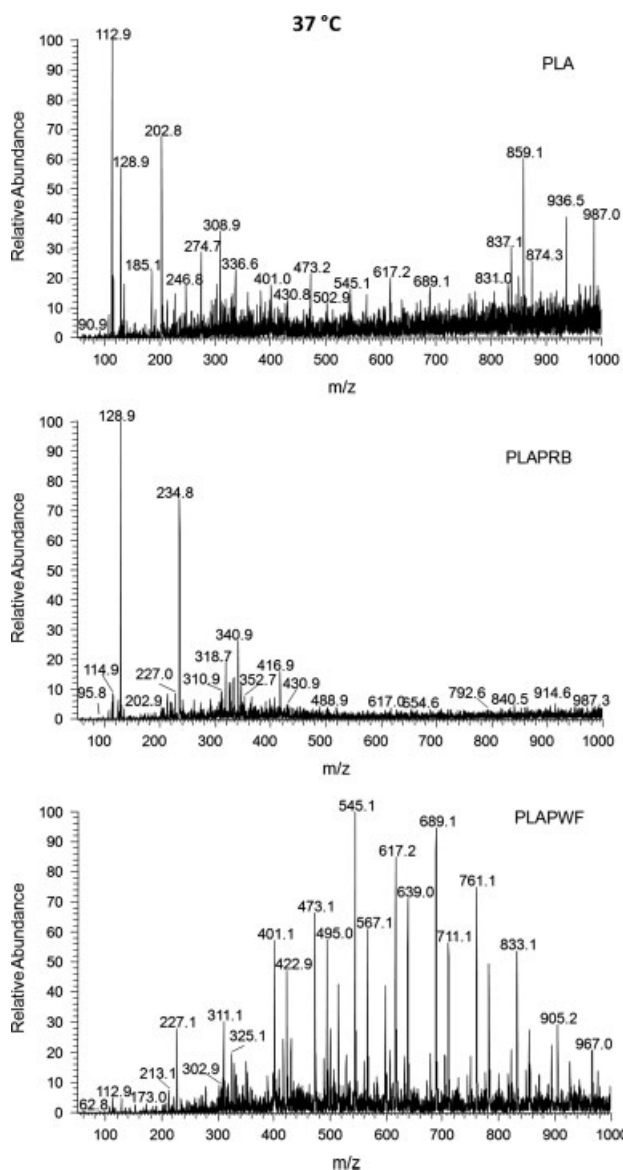


Figure 8. ESI-MS spectra showing the water-soluble migrants from PLA, PLAPRB and PLAPWF after 28 days of hydrolysis at 37 °C.

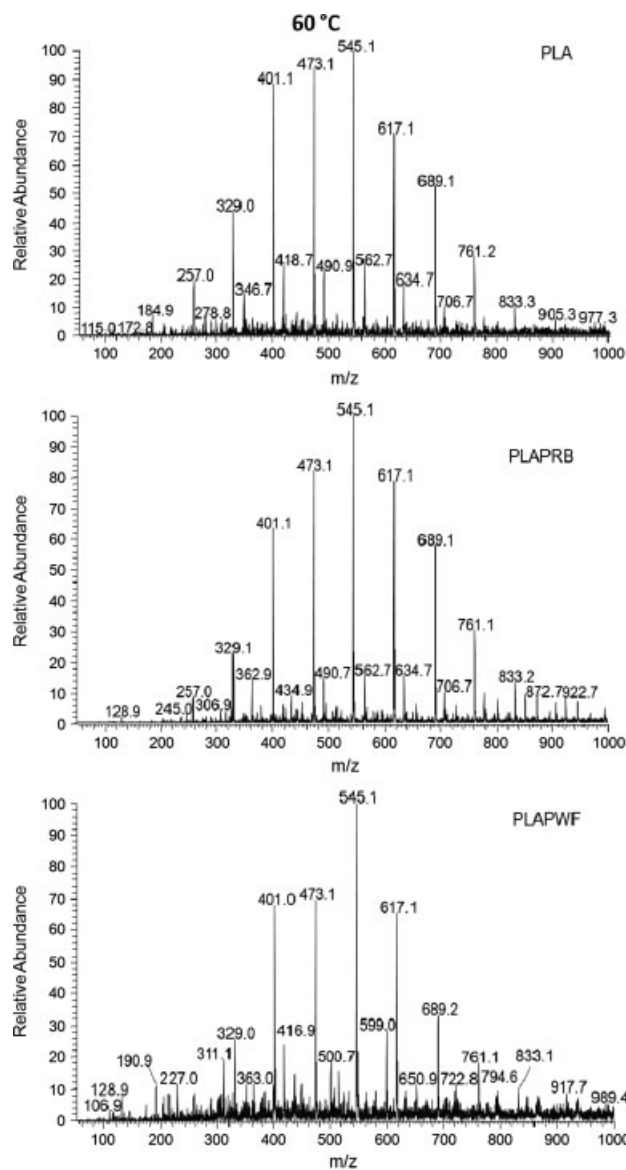


Figure 9. ESI-MS spectra showing the water-soluble migrants from PLA, PLAPRB and PLAPWF after 28 days of hydrolysis at 60 °C.

water-soluble products from the materials. Figures 6 and 7 show the weight loss of the different materials during hydrolytic aging at 37 and 60 °C, respectively. During aging of the materials at 37 °C the weight loss of pure PLA was only a few percent at the end of the aging period of 84 days. The weight loss of PLAPRB10 was rather similar to that of pure PLA. The weight losses of PLAPWF10 and PLAPWF30, on the other hand, were approximately 10 and 30% larger, respectively, compared with pure PLA.

Considerable increase in the weight loss rate was observed when the hydrolysis temperature was raised to 60 °C. The films experienced 60–70% weight loss during the aging period. The differences between the different materials were not as clear due to the possible combined effect of plasticizer migration and hydrolysis of PLA chains. Different amount of hydrolyzable PLA matrix in the different materials further complicates the situation. Due to fragmentation of the PLA films, it became more difficult to accurately determine the weight losses. The samples started to crack and fragment already during the first week of aging at 60 °C,

while fragmentation took place first between 28 and 56 days at 37 °C.

ESI-MS analysis of the water-soluble migrants from PLAPWF and PLAPRB

The influence of the new plasticizers on the water-soluble product patterns was also evaluated. The higher weight loss results obtained for PLAPWF10 and PLAPWF30 during aging at 37 °C could indicate complete migration of the wood flour based plasticizers from the films. However, the ESI-MS analysis of the migrants showed that this was not the case. Figure 8 shows the ESI-MS spectra of the migrants from the different materials after 28 days of aging at 37 °C. In the case of PLA and PLAPRB it is clearly seen that the amount of PLA hydrolysis products as well as PRB based migrants was below the detection limit and only traces of lactic acid could be observed at m/z 113 (Na-adduct of lactic acid) (Fig. 8(a) and 8(c)). However, the addition of PWF accelerated the hydrolytic degradation rate of PLA and a homologous series

of lactic acid oligomers was detected after aging of PLAPWF (Fig. 8(b)). The main series of peaks at $m/z = 18 + 72n + 23$ correlates with the Na-adducts of lactic acid oligomers. The larger weight loss is, thus, mainly attributed to faster PLA hydrolysis in the presence of PWF. The lower glass transition temperature probably to a large extent explains the faster hydrolysis of PLAPWF films. PLAPWF10 and PLAPWF30 were both above the glass transition temperature during aging at 37 °C, while the remaining films were below the glass transition temperature at this temperature. The hydrolysis catalyzing effect of free hydroxyl groups is well known and remaining un-reacted hydroxyl groups in the plasticizer could further accelerate the hydrolysis rate. Even though PRB was shown to contain a larger number of hydroxyl groups its catalytic effect would be expected to be lower due to immiscibility and phase separation of PRB resulting in limited contact with PLA matrix. After 28 days of aging at 60 °C a homologous series of lactic acid oligomers migrated from all the materials (Fig. 9). In addition to lactic acid oligomers, no other major compounds were detected in the aging water.

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