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Pyrolysis-GC–MS reveals important differences in hydrolytic degradation process of wood flour and rice bran filled polylactide composites

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ABSTRACT

Pyrolysis-GC–MS of polylactide (PLA) biocomposites before and after hydrolytic degradation revealed prominent differences in the hydrolytic degradation process of rice bran and wood flour filled biocomposites. The water uptake and mass loss for polylactide/wood flour composites were similar to that of plain PLA. Pyrolysis-GC–MS, however, showed that on prolonged ageing the hydrolysis of PLA led to increased wood flour concentration in the remaining biocomposite matrices. In contrast, the polylactide/ rice bran composites exhibited larger water uptake and higher mass loss. Pyrolysis-GC–MS and FTIR analysis proved that the higher mass loss was caused by migration of rice bran from the composites. The type of natural filler could thus greatly influence the degradation process and/or the stability of the materials in aqueous or humid environments.

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1. Introduction

Eco-friendly and degradable polylactide (PLA) has generated great interest as one of the most innovative materials for wide range of applications [1]. The addition of natural fibres or fillers in PLA provides an interesting alternative for production of low cost and ecologically friendly composites [2]. The advantages include possibilities to utilise different agricultural waste products, which could reduce the price of PLA at the same time as the material properties are improved. Reproducibility, low thermal stability and hydrophilic nature of the natural fibres which could increase the moisture absorption, cause swelling and decrease the compatibility between the fibre and hydrophobic polymer matrix, on the other hand, are some of the challenges [3].

PLA/wood fibre or PLA/wood flour composites, especially their mechanical properties and compatibilisation have been studied by several authors [4,5]. Tensile strength of PLA/wood flour composites was almost independent of wood flour content, which was suggested to be due to weak adhesion between PLA matrix and wood flour [6]. The modulus of the PLA/wood fibre composites on the other hand has been found to be comparable

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to that of PP/wood fibre composites and significantly higher than those of virgin resins [7]. PLA has also been blended with many other natural fibres such as flax [8,9], jute [10] and kenaf [11]. The use of agricultural waste as a filler in biomaterials is a highly interesting possibility. However, the chemical composition of waste products usually varies, which could cause problems in ensuring reproducible quality. Interesting results were obtained when PLA based green composites were prepared from different agricultural residues, such as wheat straw, corn stover, soy stalks and their hybrids [12]. The hypothesis of the authors was that agricultural residues contain similar amounts of cellulose-based fibres and the combination of different fibres could provide synergy effects. The study showed that similar properties were obtained by using much cheaper agricultural residues instead of agricultural fibres.

All the material modifications affect the degradability and degradation rate of PLA and other degradable materials [13]. The effect of natural fillers on biodegradation rate has so far been evaluated in a few studies [14]. The effect of wood flour on biodegradation of PLA biocomposites was studied under controlled conditions according to AS ISO 14855 [15]. The results showed that PLA/wood flour composites degraded at slower rate than the positive cellulose control, but somewhat faster than pure PLA. SEM images indicated rather poor adhesion between PLA and wood fibre, which could enhance the water penetration and bacteria





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growth and make the interface more susceptible to degradation. Another study showed that coir fibres played a minor role during biodegradation of PLA as similar CO₂ levels were observed from materials with or without coir fibres [16]. Compatibilisation, however, decreased the CO₂ formation. Biofilm was formed on the surface of PLA/wood fibre composites after exposure to fungi and algae in a microenvironment chamber [17]. The detected bulk changes indicated that the degradation of PLA matrix proceeded simultaneously with the degradation of wood fibres. The addition of wood fibres increased the microbial colonisation probably due to the increased material hydrophilicity, which also enhanced the water uptake [18].

Previous hydrolysis studies of different PLA modifications have clearly shown that hydrophilic [19,20] and hydrophobic [21] material modification can significantly affect the abiotic hydrolysis rate and also the resulting migrants and degradation product patterns [22]. While the hydrolytic degradation of PLA has been rather extensively studied [23–25], the effect of natural fibres on the hydrolytic degradation rate of PLA or other degradable polymers has so far only been investigated in a few studies [26]. Our hypothesis was that the hydrolysis process could be significantly influenced not only by the presence of natural filler, but also by the type of filler. The fate of the natural fillers themselves i.e. whether they are released to the ageing medium or concentrate in the polymer matrix, is also an important aspect that has not been investigated previously.

2. Material and methods

2.1. Materials and chemicals

Polylactide (PLA) was NatureWorks PLA, 5200 D. Chloroform was HPLC grade from Fisher scientific. The fibre fillers rice bran (RB) and wood flour (WF) were purchased from an Indonesian farmer and milled to fine powder.

2.2. Preparation of the PLA films

PLA biocomposite films were prepared by solution casting. 3.5 or 4.5 g of PLA was dissolved in approximately 75 mL of chloroform and mixed with 1.5 or 0.5 g (10 or 30 wt%) of wood flour or rice bran flour. The solution was heated under magnetic stirring on a hot plate Haake Rheocord 600 at 45 °C for 1 h. The solution was then casted on a petri dish and allowed to air-dry at room temperature overnight. Afterwards the films were dried in vacuum oven at room temperature for 1 week to remove the remaining chloroform. The samples were denoted PLAWF10, PLAWF30, PLARB10 and PLARB30 according to their composition.



Fig. 1. Water uptake of the PLA biocomposites as a function of hydrolysis time at 37 °C.



Fig. 2. Water uptake of the PLA biocomposites as a function of hydrolysis time at 60 °C.

2.3. Hydrolysis study

Each material was hydrolyzed at two different temperatures for four different hydrolysis times. For each time and temperature triplicate samples were prepared. Hydrolysis temperatures were 37 °C and 60 °C and hydrolysis times were 7 days, 28 days, 56 and 84 days. For each sample approximately 15 mg of PLA film was put into a glass vial together with 5 mL of de-ionized water and the vials were sealed with butyl/PTFE septa. The samples were put into the ageing ovens and three samples of each material were taken out after each ageing time and temperature. The remaining PLA piece was removed from water, dried on the surface and weighted for the wet weight. The pieces were then put into vacuum oven for 1 week to remove the absorbed water and then weighted again to get the dry weight. Weight loss and water absorption were calculated from the following equations:

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

 $\begin{array}{l} \mbox{Mass loss} \, = \, [(\mbox{original weight} - \mbox{dry weight})/\mbox{original weight}] \\ \times \, 100\% \end{array}$

2.4. Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of the films were recorded by a FTIR spectrometer (Perkin Elmer Spectrum 2000) in the range 4000–650 cm⁻¹. The FTIR was equipped with a single reflection attenuated total reflectance (ATR) accessory (golden gate) from Graseby Specac.



Fig. 3. Mass loss of the PLA biocomposites as a function of hydrolysis time at 37 °C.



Fig. 4. Mass loss of the PLA biocomposites as a function of hydrolysis time at 60 °C.

2.5. Pyrolysis-gas chromatography-mass spectrometry (Pyrolysis-GC-MS)

Pyrolysis-GC–MS analysis was performed by a Thermo Trace GC Ultra coupled to a Thermo Trace DSQ from Thermo Scientific and CDS 100 Pyroprobe. The column was first hold at 40 °C for 1 min, then heated at 20 °C/min to 330 °C and hold there for 10 min. The pyrolysis temperature was 500 °C. Column was Restek Rxi-5ms/ 15 m/0.25 mmID.

2.6. Mechanical properties

Mechanical properties were measured by using an Instron Universal testing machine (Model 5566) equipped with pneumatic grips and Instron series IX software (Bristol, United Kingdom). Five specimen with rectangular shape (80.5 mm^2) were prepared of each material by EP 04/80.5 mm² specimen cutter (Elastocon AB, Sweden) and conditioned at $50 \pm 5\%$ RH, 23 ± 2 °C. The thicknesses of specimens were measured by using a thickness metre. The tests performed with 500 N load cell with the cross head speed 4 mm/min.

2.7. Scanning electron microscopy (SEM)

SEM analyses were performed on a Ultra-High Resolution FE-SEM (Hitachi S-4800). The film pieces were mounted on bronze stubs using a double-sided tape and then coated with a layer of gold-palladium before the SEM analysis.

3. Results and discussion

The effect of natural fillers, wood flour and rice bran on hydrolytic degradation of PLA was investigated by following the mass loss and surface changes. The compositional changes during hydrolysis were evaluated by pyrolysis-GC–MS to determine the fate of the natural fillers during the hydrolytic ageing.



Fig. 5. Pyrograms of (a) PLARB30, (b) PLARB30 after 56 days at 37 °C, (c) rice bran and (d) polylactide. The arrows indicate compounds originating from rice bran.



Fig. 6. Pyrograms of (a) PLAWF30, (b) PLAWF30 after 56 days at 37 °C and (c) wood flour. The arrows indicate compounds originating from wood flour.

3.1. Water absorption

The addition of rather hydrophilic natural fillers could increase the water absorption of PLA, which in turn could lead to faster hydrolysis rate. The water uptake by the PLA biocomposites as a function of hydrolysis time is shown in Figs. 1 and 2. During ageing at 37 °C the water absorption of the films increased rather rapidly to 20-30% and continued then increasing to 30-50% during 84 days (Fig. 1). There were no large differences between pure PLA and PLA filled with 10 or 30 wt% of wood flour. However, the water uptake values for PLARB materials and especially PLARB10 with 10 wt% rice bran were significantly higher. The higher water uptake of the rice bran filled PLA composites was even more clearly observed during hydrolysis at 60 °C, where the water absorption of both PLARB10 and PLARB30 was considerably higher compared to the water absorption of PLAWF10 and PLAWF30 (Fig. 2). After 84 days the water absorption of rice bran composites was over 200%, while the water absorption of pure PLA and wood flour composites was only around 100%. It should, however, be noted that the measured water uptake values for rice bran composites could be somewhat overestimated because the hydrolytic ageing of rice bran composites led to the formation of porous structures (see Section 3.4) where some water could be trapped.

3.2. Mass loss

Figs. 3 and 4 show the mass loss of the materials during hydrolysis at 37 °C and 60 °C. Generally the mass losses correlated well with the water uptake of the samples, i.e. similar mass losses were observed for PLA, PLAWF10 and PLAWF30, while the mass loss for rice bran composites was somewhat higher. This was especially clear during ageing at 37 °C, where the mass loss of PLA and PLAWF10 was only around 5% after 84 days. The higher wood flour content of 30 wt% increased the mass loss to 12%. This can be compared to 22% mass loss for PLA matrix proceeded much faster and the differences were not as clear. However, the mass loss of PLA and PLAWF10 were again rather similar, while the mass loss of PLA while the mass loss of PLA content in this material. Even at 60 °C the rice bran composites degraded faster compared to pure PLA and wood flour composites.

3.3. The fate of the natural fillers during hydrolytic ageing

The total mass loss of the composites depends on the hydrolytic degradation of PLA matrix and the fate of the natural fillers i.e. whether they are released into ageing water or concentrate in the remaining polymer matrix. The natural fillers could also accelerate the hydrolytic degradation of PLA matrix due to increased water absorption and possible catalytic effect of the hydroxyl groups. Pyrolysis-GC-MS analysis of the composites before and after hydrolytic degradation revealed important differences in the hydrolytic degradation process of rice bran and wood flour biocomposites. Fig. 5 shows the pyrograms of PLARB30 before and after hydrolytic degradation as well as the pyrograms of rice bran and PLA alone. The pyrogram of unaged PLARB30 clearly demonstrates a mixed chromatogram with compounds originating both from PLA and rice bran (Fig. 5a). However, in the pyrogram of hydrolytically aged PLARB30 most compounds originating from rice bran have disappeared or are present at clearly lower concentration. This demonstrates a compositional change due to migration of rice bran components into the ageing water and explains the reason for larger mass loss in the case of PLARB composites. The opposite was observed in the case of PLAWF composites (see Fig. 6). The pyrograms of PLAWF30 before and after hydrolytic ageing show that the



Fig. 7. FTIR spectra of PLARB10 originally and after 28 days at 37 °C showing the migration of rice bran components to the surface of the composites.

relative concentration of several compounds originating from wood flour have increased i.e. the wood flour concentration in the biocomposites increases during the ageing due to the hydrolysis of PLA matrix. This correlates well with the mass loss results showing similar or slightly lower mass loss compared to pure PLA. The lower mass loss is being deduced to the stability of the wood flour and lower PLA content in the biocomposites.

3.4. Surface changes caused by hydrolysis

Changes in the functional groups and composition on the surface of the films were also followed by FTIR. During hydrolysis the FTIR spectra of PLAWF composites remained rather constant. However, in accordance with the pyrolysis-GC-MS results clear changes were observed in the FTIR spectra of PLARB composites. The changes can be attributed to the migration of rice bran components first onto the surface of the PLA films and then into the ageing water. Figs. 7 and 8 show the appearance of OH- absorption band at around 3285 cm⁻¹ after 28 days of ageing, showing the increasing concentration of rice bran components on the surface. In addition two bands appeared at approximately 1642 and 1546 cm⁻¹. These bands probably originate from the migration of the proteins present in the rice bran to the surface of the PLA films and could be assigned to amide I and amide II, respectively. These bands were more prominent with larger rice bran content in the materials. In accordance with other results the surface of PLARB composites turned to rough and porous after the hydrolytic degradation probably due to the migration of rice bran from the materials, see Fig. 9.

3.5. The effect of natural fillers on the mechanical properties

Looking at the mechanical properties of the films, the addition of 10 wt% wood flour or rice bran clearly improved the elongation at



Fig. 8. FTIR spectra of PLARB30 originally and after 28 days at 37 °C showing the migration of rice bran components to the surface of the composites.



Fig. 9. SEM images of PLARB30 (a) before hydrolysis and (b) after 28 days at 37 °C.

break, which increased by several hundred percent compared to pure PLA after addition of 10 wt% wood flour and rice bran, respectively (Fig. 10). At higher filler content the elongation at break decreased to a value just slightly above that of pure PLA. The tensile strength of the films on the other hand decreased somewhat



Fig. 10. Strain at break for the PLA biocomposites.



Fig. 11. Tensile strength for the PLA biocomposites.

compared to pure PLA films (Fig. 11). This is deduced to the inadequate adhesion between the wood flour, rice bran and polylactide matrix. The composite with highest tensile strength was the one containing 10 wt% rice bran. However, the tensile strength again decreased when rice bran content was increased to 30 wt%. An opposite trend with slight increase in tensile strength at higher wood flour content was observed for the wood flour composites.

4. Conclusions

There were significant differences in the hydrolytic degradation of rice bran and wood flour filled PLA. The addition of rice bran increased the water absorption of the materials and accelerated the mass loss rate, while the wood flour composites degraded at rather similar rate compared to pure PLA. FTIR and pyrolysis-GC–MS revealed that the composition of PLA/wood flour composites remained relatively constant with some concentration of wood flour during later stages of hydrolysis. The rice bran on the other hand migrated from the composites into the ageing water, resulting in larger mass loss and decreasing rice bran concentration in the remaining PLA matrix.

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