

# Stability Studies on Blends of a Lactic Acid-Based Hot Melt Adhesive and Starch

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Received 22 November 2007; accepted 5 April 2008

DOI 10.1002/app.28605

Published online 20 August 2008 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The stability of 70 : 24 : 6 w/w/w blends of a lactic acid-based hot melt adhesive (LHM), oxidized potato starch (dried or nondried), and polyethylene glycol (PEG) was studied. Pure LHM was used as a reference material. The methods used included tensile testing, water absorption, and scanning electron microscopy (SEM). During the ageing period of 56 days at ambient conditions ( $23 \pm 1^\circ\text{C}$  and  $42 \pm 4\%$  RH), the tensile properties of the blends were close to each other, and all of the studied materials had relatively low Young's moduli, compared to reported PLA-starch blends. In the water absorption

experiment ( $23 \pm 1^\circ\text{C}$ ), the blends reached significantly higher maximum values than the LHM. The blends also started to disintegrate already after 3 days in water, while the water absorption of pure LHM could be studied for 49 days without detectable disintegration. The SEM images showed that the tensile testing fractures occurred via the continuous LHM matrix in the blends. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2467–2474, 2008

**Key words:** poly(lactic acid); biodegradable; hot melt adhesives; blends; degradation

## INTRODUCTION

Hot melt adhesives are thermoplastic materials that are applied in the molten state onto the desired surface of one or two objects, after which the objects are united. The adhesive bonds are formed as the adhesive cools down. The application area of hot melt adhesives is vast, including for example carton and case sealing, paper industry, and bookbinding.<sup>1,2</sup> As the regulative pressure for moving towards degradable or reusable packaging increases,<sup>3</sup> there is a growing interest in hot melt adhesives that not only have adequate technical properties for the desired application, but also meet the requirements related to biodegradability. Combinations of biodegradable and nonbiodegradable materials are in general not recommended, since the packaging in that case cannot be considered biodegradable as a whole.<sup>4</sup> Separating the different parts for recycling is not always a feasible option either. An additional advantage of biodegradable polymers as hot melt adhesives is that many of them can be produced from renewable raw materials.<sup>5</sup>

Studies on lactic acid-based hot melt formulations have been reported in a few scientific papers in the recent years. They have been shown to be promising with relation to their technical properties,<sup>6–8</sup> and their degradation rates have been found sufficient in hydrolytic and composting environments.<sup>9</sup> Also the relationships between the composition and the properties of such polymers have been studied.<sup>10</sup> However, lactic acid-based hot melt adhesives tend to degrade very quickly during storage at ambient conditions and concurrently lose their mechanical and adhesive properties. One of the main challenges in their development is thus studying and tailoring their storage stability in order for the material to be stable enough during storage, but to degrade quickly upon disposal or during repulping. It has also been suggested that polylactide based paper coatings would be advantageous compared to for example polyethylene in paper repulping, since polylactide is more easily separated in the process, and the waste can be easily recycled or composted.<sup>11,12</sup>

The long-term stability and properties of polymers can be affected by both physical and chemical ageing. Physical ageing involves changes in the chain arrangements of the polymer without any chemical modification. This leads to changes in for example the mechanical properties such as brittleness and tensile strength, or the glass transition temperature.<sup>13</sup> Chemical ageing, however, leads to degradation of the polymer and is thus a nonreversible process, which causes deterioration of polymer quality in terms of for example its mechanical properties. Typi-

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Contract grant sponsor: Kiilto Oy.

cal reactions related to chemical ageing are for example chain-scission and depolymerization.<sup>13</sup> Both chemical and physical ageing are time and temperature dependent.

Until now, no scientific papers have concentrated on blending of starch with a lactic acid-based hot melt composition in particular, although blends of poly(lactic acid) with different types of starch have been studied in several scientific publications.<sup>14–33</sup> Starch is a cheap commodity polymer that can be isolated from cereals and root crops. As a blend component, it decreases the price of the material as a filler and additionally provides a means to affect for example the mechanical properties or the biodegradation rate of the blend. However, lactic acid-based polymers are thermodynamically immiscible with starch due to the hydrophobicity of the lactic acid-based polymer and the hydrophilic nature of the starch. This leads to high interfacial tension and weak mechanical behavior in uncompatibilised blends,<sup>19,24–28,30–32</sup> although it is possible that weak hydrogen bonding between the carbonyl in PLA and the hydroxyl groups in starch exists.<sup>18</sup>

The objective of this study was to evaluate the stability of a lactic acid-based hot melt formulation blended with a H<sub>2</sub>O<sub>2</sub> and NaOCl oxidized potato starch in both its dried and nondried state. To improve the interfacial adhesion between the carboxyl-terminated LHM and the oxidized starch, PEG400 was used as a compatibiliser in the blends. PEG400 is biocompatible and it has also been reported to be a suitable plasticizer for PLA.<sup>29,33</sup> Changes in the mechanical properties of the materials stored at ambient conditions were studied by tensile tests for a period of 56 days. Water absorption measurements were conducted for immersion periods of 10 and 49 days on the starch blends and pure LHM, respectively. Since the mechanical properties of a material are closely related to its microstructure, changes in the morphology of the tensile testing specimens were also followed by scanning electron microscopy (SEM) for pure LHM and the blend with dried starch. Additionally, the effect of different crosshead speeds on the tensile properties of pure LHM was evaluated after a conditioning period of 1 day.

## EXPERIMENTAL

### Materials

The hot melt formulation (LHM) was prepared and delivered by Hycail b.v., The Netherlands. It was a carboxyl-terminated branched polycondensate based on lactic acid and flexibilising components. The starch used was provided by Ciba Specialty Chemicals OY, Finland. It was a H<sub>2</sub>O<sub>2</sub> and NaOCl oxidized

potato starch with a moisture content of 10%, as determined. The compatibiliser used was polyethylene glycol (PEG400, Fluka). The blends consisted of LHM, starch (dried or nondried), and PEG in a 70 : 24 : 6 w/w/w ratio.

### Methods

#### Blending and film preparation

The materials were processed in a kneader (Rheomix 600, Haake, Paramus, NJ) at 180°C ± 5°C and 60 rpm for 5 min, in batches of ca. 40 g. The molten material was pressed between two glass sheets covered with silicone paper immediately after the processing. An even film thickness was achieved by placing four pieces of metal wire with a thickness of 0.80 mm in the corners of the glass sheets. The test specimens used in the tensile tests and the water absorption experiments were cut from the films on the day of the processing.

#### Analysis methods

The fourier-transform infrared (FT-IR) measurements were conducted with Perkin-Elmer (Bucks, United Kingdom) Spectrum One FT-IR accessory, by using the ATR method. The scan number and the instrument resolution were 16 and 2 cm<sup>-1</sup>, respectively.

The tensile testing method used was the modified ASTM D638-81.<sup>34</sup> The tensile testing machine used was Lloyd Instruments LRX, Fareham, United Kingdom, with a gauge length of 20 mm and a crosshead speed of 10 mm/min. The test specimens were rectangular with the dimensions of 15 mm × 50 mm. The materials were tested after 1, 7, 14, 28, and 56 days, and the starch blends additionally after 42 days. The temperature and the relative humidity were monitored during the storage and they were 23 ± 1°C and 42% ± 4%, respectively. To study the effect of crosshead speed on the stress and strain values, experiments were conducted on pure LHM with crosshead speeds of 10, 25, 50, 100, and 150 mm/min after 1 day of ageing. The tensile testing results reported are averages of a minimum of five replicates.

The water absorption test method used was the modified ASTM D570-81.<sup>35</sup> The water absorption experiments were started on the day of the processing; the test specimens were immersed in distilled water in plastic containers at ambient temperature (23 ± 1°C) directly after the sample preparation. After specific intervals, the test specimens were removed from the containers, gently blotted with tissue paper to remove the excess water from the film surface, and weighed. Water absorption was deter-

**TABLE I**  
Wavenumbers Related to the Groups of Hydrogen Bonds in the FT-IR Spectra of Pure LHM and the Blend Containing Nondried Starch

Material	Vibration wavenumber ( $\text{cm}^{-1}$ )		
	—C=O carbonyl peaks	—O— in —CH—O—	—C—O— in —O—C=O
LHM	1756, 1751, 1749	1184	1128, 1086, 1044
Blend containing nondried starch	shoulder, 1750, 1749	1183	1126, 1085, 1044

mined gravimetrically based on initial weight in three replicates at each immersion period.

The microstructures of the fractured specimens from the tensile tests were observed using JSM-5500 and JSM-6335F (JEOL, Tokyo, Japan) scanning electron microscopes.

The starch drying and moisture content determination method used was the modified American Association of Cereal Chemists method 44-15A<sup>36</sup>; the starch was dried in a laboratory convection oven at 130°C for 2 h, cooled down in a desiccator and weighed after this. The method yields starch with a moisture content of approximately 0.5%.

## RESULTS AND DISCUSSION

### Appearance of the films

The films containing pure LHM were thicker ( $\sim 3.0$  mm) than the films containing starch ( $\sim 1.5$  mm), indicating differences in their flowing behavior. The film containing pure LHM also became thicker in places during the storage period. Similar changes in the thickness of the film were not observed for the films containing starch, indicating significant morphological changes due to the blending process.

### FT-IR Spectroscopy

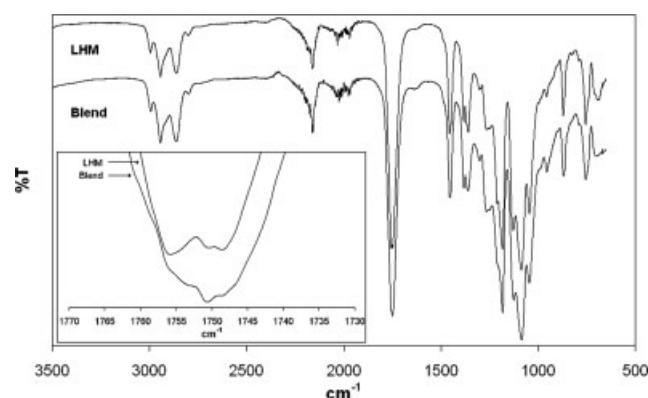
Miscibility of the blend components was confirmed by comparing the spectra for the LHM and the blend containing nondried starch. It has been shown that in incompatible blends, no significant changes should be seen in the IR-spectra of the main blend component before and after blending.<sup>37</sup> In compatible blends, however, peak broadening and shifting should occur.<sup>37,38</sup>

The wavenumbers of the groups involved in the hydrogen bonds of the blend and the LHM can be found in Table I. The FT-IR-spectra for these two materials are presented in Figure 1, where the region near the C=O carbonyl peak is shown in the insert. As can be seen from Figure 1, the C=O carbonyl peak of the LHM at  $\sim 1750$   $\text{cm}^{-1}$  consisted of three components. Splitting of this PLA carbonyl peak has been discussed in other publications,<sup>38</sup> but the reason for it was not investigated in more detail in this

study. When comparing the C=O region of pure LHM and the blend at  $\sim 1750$   $\text{cm}^{-1}$  (Fig. 1), peak broadening and shifting to lower wavenumbers was observed. It can also be mentioned that the starch and the PEG used did not have peaks in this wavenumber range. Also the peaks observed for LHM at 1184  $\text{cm}^{-1}$  (—C—O— in —CH—O—), 1128  $\text{cm}^{-1}$ , and 1086  $\text{cm}^{-1}$  (—C—O— in —O—C=O) shifted slightly to lower wavenumbers. Although the changes in the wavenumbers of the peaks were relatively small, the results obtained suggest compatible blend formation. Similar peak shifting has been observed for blends of PLA and starch by others.<sup>18</sup>

### Tensile tests

The mechanical properties of the materials during storage under ambient conditions were followed in terms of stress and strain at maximum load (Table II) and Young's modulus (Fig. 2). The stress values obtained were in general significantly lower compared to reported values for PLA or PLA-starch blends with similar or lower amounts of plasticizer, while the strain values were higher than the reported ones.<sup>14–19,24,26–32</sup> This, however, can be related to the fact that although the LHM had a very high molar mass (a molar mass of over 800,000 g/mol was determined in a separate study), it had a crosslinked structure and also contained a flexibilis-



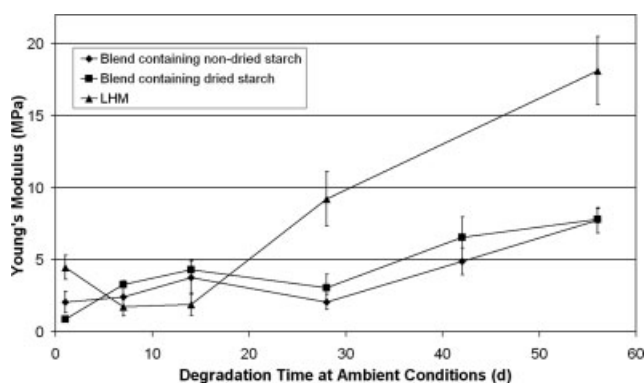
**Figure 1** FT-IR spectra of pure LHM and the blend containing nondried starch. The spectra have been shifted vertically in relation to each other. The C=O carbonyl peaks of the materials at  $\sim 1750$   $\text{cm}^{-1}$  can be found in the insert.

**TABLE II**  
**Stress and Strain at Maximum Load Values of Pure LHM**  
**and the Starch Blends at the Ageing Periods Tested**

Test day no.	Blend Composition		
	LHM	Blend containing nondried starch	Blend containing dried starch
	Stress at maximum load (MPa) [Strain at maximum load (%)]		
1	0.08 ± 0.01 (53.1 ± 26.3)	0.07 ± 0.00 (34.8 ± 3.6)	0.08 ± 0.00 (34.2 ± 1.5)
7	0.03 ± 0.01 (58.8 ± 28.1)	0.13 ± 0.01 (18.7 ± 2.6)	0.13 ± 0.01 (20.5 ± 4.0)
14	0.04 ± 0.01 (29.0 ± 9.2)	0.17 ± 0.01 (14.8 ± 1.3)	0.18 ± 0.01 (14.2 ± 1.6)
28	0.24 ± 0.05 (23.2 ± 2.6)	0.21 ± 0.01 (12.2 ± 1.1)	0.24 ± 0.02 (11.9 ± 3.2)
42	–	0.20 ± 0.01 (9.8 ± 0.8)	0.20 ± 0.01 (9.3 ± 1.5)
56	0.61 ± 0.06 (16.2 ± 3.2)	0.21 ± 0.01 (8.4 ± 0.9)	0.20 ± 0.01 (8.7 ± 0.9)

ing component, in addition to the lactic acid-based part. It can also be mentioned that high strain values have been obtained in the reported studies for PLA-starch blends that contain higher amounts of plasticizers such as for example acetyl triethyl citrate.<sup>22</sup>

The stress at maximum load of pure LHM decreased slightly during the first 7 days. After 14 days of ageing, the stress values increased virtually linearly for pure LHM until the end of the experimental period, while the strain at maximum load increased slightly during the first week and decreased after this. The crystallinity of PLLA has been reported to increase as the amorphous regions of the polymer are hydrolytically degraded, with a concurrent decrease in mechanical strength.<sup>39</sup> This could explain the initial decrease in stress during the first 7 days of ageing. However, by contrast to the aforementioned typical behavior of standard PLLA and in accordance to the results obtained in this study, increasing trends in stress together with decreasing strain have been reported also for other biodegradable hot melt adhesive compounds during ageing at ambient conditions.<sup>8</sup> The stiffness of the LHM increased towards the end of the degradation period, which was demonstrated in the trend of Young's modulus for this material.



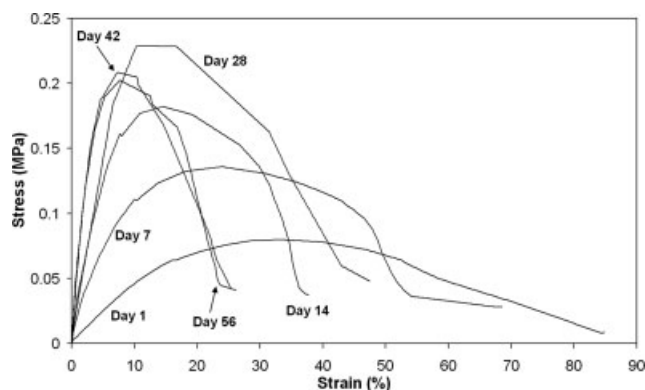
**Figure 2** Young's moduli of pure LHM and the starch blends versus degradation time at ambient conditions.

The stress at maximum load values of the blends increased up to day number 28 and remained at a relatively constant level after this. The blend containing dried starch had a slightly higher maximum stress value than the blend containing nondried starch. There were no large differences between the mechanical properties of the blends during the degradation period otherwise. This is in agreement with results obtained for PLA-starch blends.<sup>18</sup> During the first 14 days, the stress values of the blends were higher than for pure LHM. After 28 days of ageing, all of the materials had approximately the same stress at maximum load, and the blends had reached their maximum values. The stress of pure LHM increased seemingly linearly after 14 days of ageing, and it was significantly higher than the stress values of the blends at the end of the ageing period. The stress values of the blends remained at a relatively constant level during the second half of the experiment. The strain at maximum load values of the blends were lower than the values obtained for pure LHM during the entire experiment.

The Young's modulus of the blends increased with degradation time, but the blend containing dried starch had slightly higher values. In general, the Young's moduli of both pure LHM and the blends were substantially lower than reported values for blends of standard PLA and starch typically.<sup>17,19</sup> This, however, originates from the fact that the composition, morphology, and hence also the tensile properties of the LHM were different compared to semicrystalline high-molecular weight PLA.<sup>40</sup>

It has been shown that due to evaporation during the processing, the final moisture content of PLA-starch blends does in fact not depend on the initial moisture content of the starch, when processing at 180°C with similar equipment.<sup>28</sup> However, since PLA depolymerises easily in the presence of water at elevated temperatures,<sup>40</sup> one of the reasons for the minor differences observed in the mechanical properties of the blends during the ageing period can

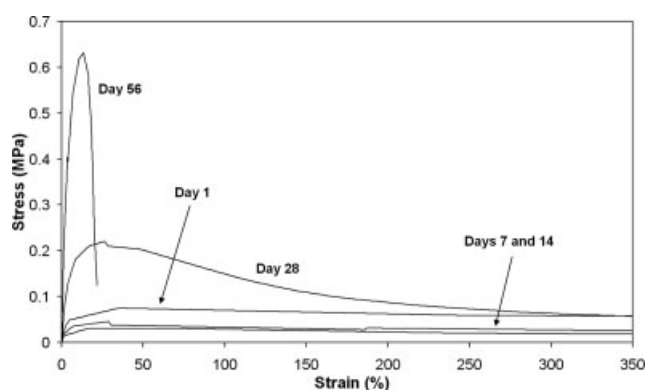




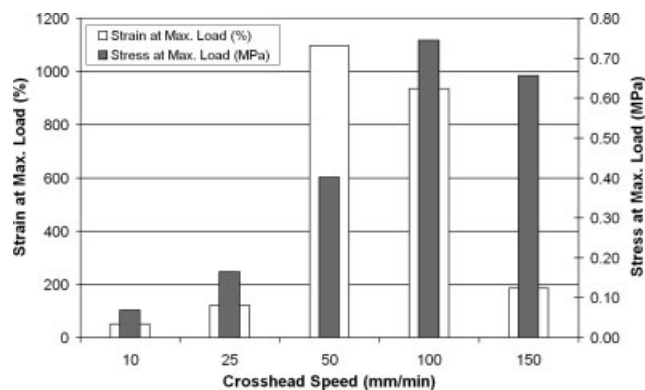
**Figure 3** Stress–strain curves of the blend containing dried starch.

have been processing related thermohydrolysis of the LHM. Nondried starch is, however, typically better dispersed in the continuous phase of the blend, resulting in higher interfacial area between the starch and the continuous matrix.<sup>18</sup> This, in turn, should increase the tensile strength of the blend and reduce the possible differences caused by thermohydrolysis.

Typical stress–strain curves of the tensile tests are shown in Figures 3 and 4. The curves for the blend containing nondried starch are not shown since they were similar to the ones obtained for the blend containing dried starch. The stress–strain curves illustrate how the blends containing starch were the only ones that broke in tension at all degradation periods. Pure LHM broke only on day number 56, and the experiments were stopped manually before fracture at the testing periods before this due to the high strain values. The reported maximum stress and strain values have therefore been taken from the first maximum occurring at the beginning of the stress–strain curve for pure LHM. However, very high strain values are in general not essential, or even de-



**Figure 4** Stress–strain curves of pure LHM.



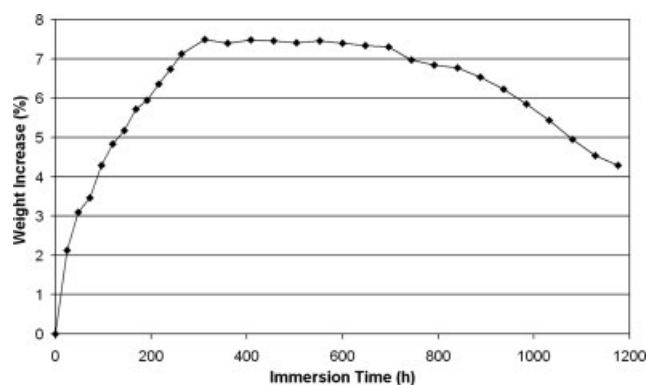
**Figure 5** Stress and strain at maximum load of pure LHM versus crosshead speed.

sirable, in hot melts used in for example packaging applications.

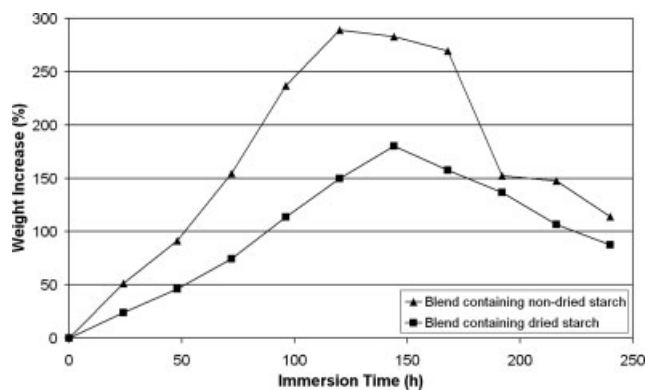
The results from the tensile tests conducted with different crosshead speeds on pure LHM showed that stress and strain at maximum load were clearly dependent on the crosshead speed used (Fig. 5). Strain at maximum load increased with crosshead speed up to 50 mm/min and started to decrease, as the crosshead speed was increased further. A similar trend could be observed for the stress values, with the exception that the highest value was obtained at 100 mm/min. This kind of phenomena with a critical value at  $\sim 100$  mm/min have been observed also for example for linear low-density polyethylene,<sup>41</sup> polypropylene, poly(ethylene terephthalate) and high density polyethylene.<sup>42</sup>

### Water absorption

The water absorption values of pure LHM (Fig. 6) were approximately in the same range as the reported values for polylactide in other studies.<sup>16,17,30,31,43</sup> However, it should be stressed that



**Figure 6** Water absorption of pure LHM versus immersion time.



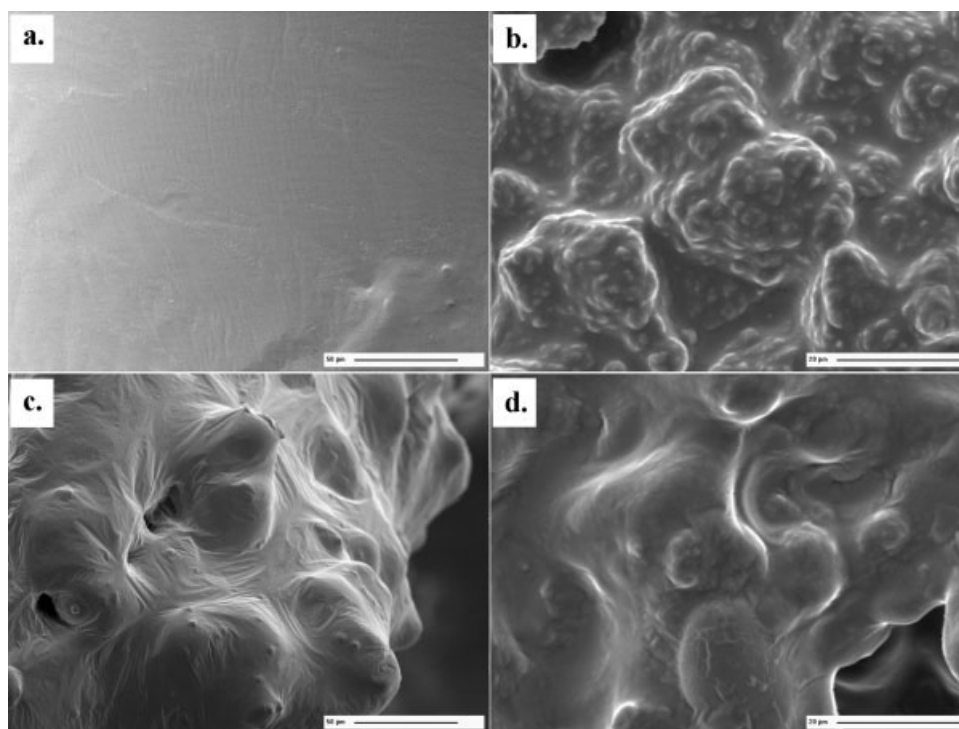
**Figure 7** Water absorption of the starch blends versus immersion time.

water absorption of a polymer is dependent on its crystallinity. The amorphous regions can absorb more moisture than the crystalline parts, and the extent of water absorption for this reason also varies for different types of polylactide. The water absorption of pure LHM reached its maximum, i.e.,  $\sim 7.5\%$ , after 13 days (312 h) of immersion in water, and remained at a relatively constant level until day number 29 (696 h). After this the weight of the film decreased steadily until the end of the immersion period. The color of pure LHM became lighter towards the end of the immersion period, especially near the edges of the film. The reason for the change in the color of the material was not verified in this study

but one possible reason for it is an increasing level of crystallization, since similar whitening caused by hydrolysis has been reported for standard polylactide,<sup>43</sup> as well as for a lactic acid-based hot melt composition,<sup>9</sup> as a result of increased degree of crystallinity.

The maximum water absorptions of the blends were 290% (120 h) for the blend containing nondried starch and  $\sim 215\%$  (144 h) for the blend containing dried starch (Fig. 7). Moisture content of starch has also been reported to increase the water absorption of PLA-starch blends in other studies.<sup>18</sup> Both of the blends started to disintegrate visibly already after 3 days (72 h). After 10 days (240 h), weighing the test specimens became impossible due to complete falling apart of the film structure. The main reason for the decreasing weight of the blends containing starch after the maximum can thus be ascribed to the loss of film pieces due to disintegration of the material. For blends of PLA and PEG it has been shown that at PEG contents of 30% and lower, the water absorption of the blend involves both degradation of PLA and dissolution of PEG.<sup>44</sup> Since the initial PEG/starch and starch/LHM ratios were 0.3 on the dry basis for both of the blends, it is unlikely that the observed differences in the water absorptions of the blends were caused by the effect of starch moisture on the initial composition of the blend containing nondried starch.

When soaked in excess water at 25°C, starch can absorb up to 50% of water on a dry basis.<sup>45</sup> There-



**Figure 8** SEM images of the materials used in the tensile tests (ageing periods in parenthesis): (a) pure LHM (2 days), (b) pure LHM (58 days), (c) blend containing dried starch (2 days), and (d) blend containing dried starch (57 days).

fore, if the maximum water absorption of LHM, as determined, is 7.5%, the theoretical maximum water absorption of the starch blends would be 16–17%. However, the actual water absorptions of the blends were significantly higher than the theoretically calculated one.

## SEM

Representative scanning electron micrographs of the fractured test specimens are presented in Figure 8(a–d) for pure LHM and the blend containing dried starch. Since actual fracture surfaces could not be obtained for pure LHM on the first days after the processing, the image taken of pure LHM in Figure 8(a) has been taken from a stretched part of the film and this has been assumed to give a representative picture of the bulk LHM. Two days after the processing, pure LHM had a smooth surface even after being stretched [Fig. 8(a)]. After a degradation period of 58 days, the LHM consisted of spherical structures [Fig. 8(b)] that were similar to the ones observed for other biodegradable hot melt compositions in composting studies.<sup>9</sup>

For the blend containing dried starch, the shapes of the starch granulates were visible under the LHM matrix after 2 days, but the continuous phase covered the granules well at this stage [Fig. 8(c)]. After 57 days, similarly to pure LHM, also the blend contained smaller spherical structures [Fig. 8(d)]. The overall microstructures of the two materials were, however, very similar at this stage, although the blend seemed to have a slightly smoother surface structure than the LHM. This, however, is in contrast to the differences observed in the mechanical behavior of the materials at the end of the ageing period.

Typically, immiscibility between starch and a biodegradable polymer matrix appears in SEM images as cracks or voids between the continuous matrix and the starch, or as loosened granulates.<sup>14,15,32,46</sup> In this study, a few minor gaps were observed within the polymer matrix in the SEM images, but not specifically in the interfacial area between the starch granulates and the matrix. This suggests that the interfacial adhesion between the starch and the polymer matrix was stronger than the internal cohesion of the LHM during the experimental period.

## CONCLUSIONS

The packaging industry is moving towards biodegradable materials that are preferably produced from renewable resources at an increasing speed. Developing materials to suit the industry's needs, not only in terms of a wide range of properties but also considering their economical feasibility, is thus becoming more and more urgent.

One of the most interesting findings of this study was that the LHM-starch blends had remarkably higher water absorptions than the lactic acid-based LHM (~ 40 times larger than for pure LHM) or reported blends of standard PLA and starch. The blends also started to disintegrate after 3 days of water absorption, by contrast to the LHM, which only whitened and underwent dissolution of low molecular weight components, even after longer immersion periods. This could be a significant advantage in for instance the disposal of single-use applications; using starch as a blend component would increase the degradation rate of the actual adhesive, whereas disintegration of the adhesive structure would allow for quicker detachment of the united objects in a compost environment. However, the materials would, for the same reason, have to be protected from moisture before disposal. To fully evaluate the suitability of the LHM-starch blends in practical applications, also adhesion tests would have to be conducted. It can in any case be concluded that blending starch with a lactic acid-based hot melt adhesive proved to be a promising alternative for tailoring the degradation properties of the material. Because of the currently high price of lactic acid-based polymers compared to conventional hot melt formulations, using starch-blends would also be economically beneficial.

The authors thank Hycail Finland Oy and Ciba Specialty Chemicals Oy for providing the materials. The authors also wish to thank Joni Korventausta from Turku Centre for Biomaterials at the University of Turku for conducting the SEM measurements.

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