

## Effect of Lignin Removal on Mechanical, Thermal, and Morphological Properties of Polylactide/Starch/Rice Husk Blend Used in Food Packaging

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**ABSTRACT:** The aim of this work was to investigate the possibility of using cost-effective natural filler in a biodegradable polymer and find new set of materials for green biocomposites to be used in food packaging. In this regard, rice husk (RH) and bleached rice husk (BRH) have been used in the form of powder and the effect of lignin removal on mechanical and thermal properties of prepared composites with poly(L-lactide) and starch were studied. Using FTIR technique, the lignin removal from RH has been approved. The tensile, Charpy impact, and hardness tests were implemented to investigate the mechanical properties. It was concluded that filler caused increase both in the toughness and the Young modulus of samples. It was also found that the lack of lignin in BRH samples improves the mechanical properties. It was clearly observed that the BRH samples show larger modulus, Charpy impact strength, and hardness compared to those filled with RH. Despite larger values for the elongations at break of RH samples, the mechanical properties showed a significant improvement (between 25 and 50% improvements) on lignin removal. The differential scanning calorimetry thermograms revealed an improvement in crystallization behavior and reduction of  $T_g$  from 47 to 31°C in the case of BRH-filled samples. Finally, due to the removal of toxic lignin in the samples and modification of mechanical properties by this method, the BRH could have the ability of wide use in the bioplastics and food packaging industries. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2014, 131, 41095.

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### INTRODUCTION

Nowadays, environmental pollutions caused by the use of nonbiodegradable polymers have lured many researchers to use biodegradable polymers in their studies.<sup>1</sup> However, biodegradable polymers cannot come to wide use as they are expensive and have physical and mechanical limitations such as their storage conditions, water absorption, interface adhesion, and brittleness observed in some polymers such as poly lactic acid (PLA).<sup>2</sup> Starch is a potentially useful material for biodegradable plastics because of its low cost and natural abundance<sup>3</sup>; conversely, starch is a brittle biodegradable polymer, has strong water absorption, and is not good for practical applications.<sup>4</sup> Thermoplastic starch that usually has been produced by conventional melt-processing has poor mechanical properties, which is mainly because of thermal degradation of starch before melting, the strong water absorption, and poor interfacial adhesion with other components.<sup>5–7</sup> To settle these

problems, starch granules were modified by the physical modification methods, such as blending and chemical modifications.<sup>8–10</sup> Natural starch exists in a granular form. The granular shape and size are different in plants. Corn starch granules are mainly spherical, whereas wheat starch contains both spherical and disk shaped granules, and potato starch has a smooth granular surface, which is mainly oval.<sup>11,12</sup> In many investigations, starch is selected to fabricate biodegradable polymer blends. One of the most common biobased polymers frequently studied is poly(L-lactic acid) (PLLA). PLLA is attractive for disposable and biodegradable plastic substitutes because of its very good mechanical properties.<sup>13,14</sup> According to previous studies, this aliphatic polyester is a good choice for blending with starch to obtain a biodegradable blend with proper physical and mechanical properties.<sup>15–21</sup>

Fillers were initially introduced to plastic industries for economic reasons. Subsequently, it was documented that, in some

cases, filler could also strengthen the mechanical modulus of a composite.<sup>22,23</sup> In fact, starch plays the filler role.<sup>24,25</sup> Natural starch has no effect on the atmospheric carbon dioxide level; it is inexpensive, available and often used as filler for thermoplastic productions.<sup>26–28</sup> The other materials which have been recently used as filler are lignocelluloses wastes. These natural fibers result in lighter final product and not only minimize the environmental pollution due to their biodegradable nature but also decrease the cost of final product. They may also improve the mechanical properties of plastics as well.<sup>29</sup> The rice husk (RH) is one of the natural fibers which are the outer covering of paddy and accounts for 20% of its weight. RH is removed by rice milling and contains cellulose (35%), hemicellulose (25%), lignin 20%, and ash 17% (94% silica) by weight. It is necessary to investigate the possibility of using RH into plastic materials to produce useful composites.<sup>30</sup> However, to use RH in food industry as filler, lignin should be removed as much as possible due to its toxicity.<sup>31–33</sup>

In the present study, PLLA–starch blend was filled with RH flour to prepare a biocomposite having suitable properties for potential application in biodegradable food plates and containers. Bleaching process is used for modification of RH behavior. Diphenyl-methane-4,4'-diisocyanate (MDI) and triethyl citrate (TC) were used as coupling agent and plasticizer, respectively. Fourier transform infra red (FTIR) technique was implemented to confirm the maximum extraction of lignin from RH. The effect of bleaching and addition of plasticizer on chemical, mechanical, and thermal properties of composites was investigated by the FTIR, tensile, charpy impact, and hardness tests and also the differential scanning calorimetry (DSC) thermograms. The scanning electron microscopy (SEM) micrographs were used for morphological studies. The main objective of this study is to use cost-effective natural filler in a biodegradable polymer as an alternative for food packaging. Due to toxicity of lignin, it must be removed from the RH. Moreover, new compositions of green composites have been introduced as potential applications for further studies.

## EXPERIMENTAL

### Materials

Technical grade corn starch was used in this study. The moisture content in the starch was about 12 wt %. It was measured by drying the starch in an oven at 105°C for 24 h. Poly(L-lactide) was prepared from 90% L-lactic acid solution (Merck, Germany) according to a research by Gilding and Reed.<sup>34</sup> Monomer (L-lactide) was purified by multiple recrystallizations from ethyl acetate and dried under vacuum at room temperature for 24 h. The catalyst, stannous octoate (Sn(Oct)<sub>2</sub>) (Sigma, St. Louis, MO), was purified by the vacuum distillation. The polymer were synthesized inside a glass ampule according to the procedure of previous study<sup>35</sup> with molecular weight ( $M_w$ ) and polydispersity index (PDI) 80,000 g/mol and 1.57, respectively. The RH, as filler, was supplied by a local mill (Guilan, Paresar). The particle size of the RH was 70–80 mesh numbers. The RH flour was dried at 110°C for 24 h to set the moisture content within 1–2%, and then it was stored over desiccant in sealed

containers. All the other chemical and solvents were the reagent grade from Merck (Darmstadt, Germany).

### Bleaching of RH

The RH powder prepared at 70–80 mesh was bleached by 4–6 wt % of sodium hypochlorite (Merck 105614) at 25°C for 30 min using a mechanical mixer at 150 rpm rotor speed. After washing the supplied material with a 2–4 wt % of the sodium hydroxide solution 1N (Merck 109137) and pure water, it was dried in an oven for 24 h at 110°C.<sup>36</sup>

### Determination of Holocellulose and Lignin Content

The holocellulose content was determined using the Wise method.<sup>37</sup> According to this method, 2 g of RH was placed in a 100-mL Erlenmeyer and 80 mL water added. Afterward, 0.25 mL acetic acid glacial 100% (Merck 100056) and 0.75 g sodium chloride (Merck 106420) were added to the previous mixture. The Erlenmeyer was sealed with a cover and was put in hot water 80°C for 1 h. Sodium chloride was added again three more times to have more accurate results. Then, the mixture was cooled down in an ice-water bath. The mixture filtered on a glass filter in a vacuum suction and the filtered sample was washed with 100 mL ice water. Finally, the sample was washed with 25 mL acetone and placed in aluminum cups and dried in oven at 105 ± 3°C for 24 h. Then, the sample was weighed after 24 h. The holocellulose percent was determined using the following equation:

$$\text{Holocellulose \%} = \frac{W_h}{W_H} \quad (1)$$

$W_h$  is the weight of holocellulose obtained from the Wise method and  $W_H$  is the weight of unmodified pure RH. The Wise method was used to determine RH and bleached rice husk (BRH) holocellulose contents which were 61 and 76%, respectively. The lignin content was determined as the acid-insoluble Klason lignin by the TAPPI T211 standard method. The classical method for the quantitative determination of lignin is based on Klason's technique involving hydrolysis with 72% sulfuric acid (Merck 1.00748 98% diluted). In this procedure, lignin is left as an insoluble residue and is recovered by filtration and gravimetrically determined.<sup>38</sup> The lignin content of RH and BRH was obtained to be 20 and 4%, respectively. The complete removal of lignin was also approved by FTIR results.

### Preparation of PLLA–Starch–RH Blends

MDI (Merck 820797) was dissolved in diethyl ether (Merck 100926) and then sprayed on starch and PLLA with an equal ratio 1 wt % of total polymer. After that, materials were dried in a vacuum oven at 50°C to evaporate the extant diethyl ether in the mixture. All materials were mixed with 50 : 50 PLLA/starch content according to previous studies<sup>39–41</sup> as shown in Table I. The mixing process was carried out using an internal mixer (Brabender, Germany) at 180°C for 15 min at the rotor speed of 60 rpm. The obtained blends were molded in 3–4-mm sheets by hot-press at 180°C applying 14 bar pressure for 5 min.<sup>39</sup>

### Characterization

The molecular weight and PDI of PLLA were determined by the gel permeation chromatography (GPC) technique using an

**Table I.** Composition of Samples (%)

Samples	PLLA	Starch	RH	BRH	MDI	TC
LASR1	42	42	5	0	1	10
LASR2	39.5	39.5	10	0	1	10
LASR3	37	37	15	0	1	10
LASR4	42	42	0	5	1	10
LASR5	39.5	39.5	0	10	1	10
LASR6	37	37	0	15	1	10
LASR7	44.5	44.5	0	0	1	10

Agilent GPC 1100 chromatograph. Chloroform was used as eluent. The temperature and flow rate in this experiment were fixed at 35°C and 1 mL/min, respectively. Two PL Mixed C columns with a Viscotek 3580 refractive index detector and an injection volume equal to 100  $\mu$ L were used. The sample molecular weight was calibrated with the standard polystyrene. All the methods mentioned above were performed according to ASTM D 6579.

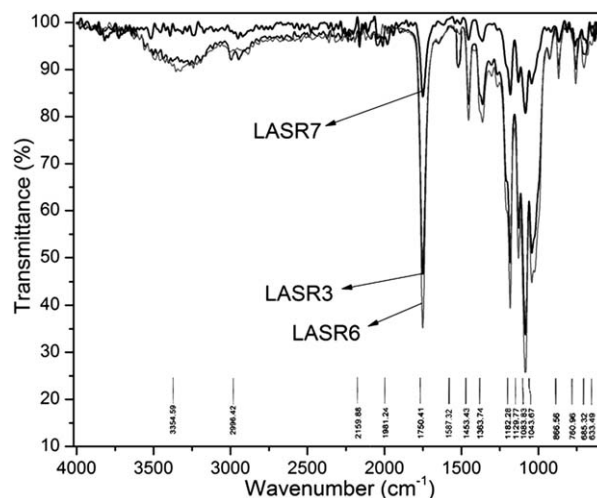
The infrared spectroscopy was performed using a Bruker instrument (Bruker, Equinox 55LS 101 series, Germany) with the resolution of 4  $\text{cm}^{-1}$  (averaging 50 scans) for determination of functional groups of polymers. The DSC was carried out using a Netzsch DSC Maia 200 F3 equipped with a low-temperature accessory. The DSC measurements were performed at a heating rate of 20°C/min, in nitrogen atmosphere and at the temperature ranged from -20 to 260°C. The glass transition temperature ( $T_g$ ) was taken at the midpoint of the stepwise specific heat increment. The repeated heating scans were performed to verify the reproducibility of the results. All the adjustments were performed according to ASTM D3418.

The stress-strain measurements were carried out on samples by means of a Gotech Universal AI-7000-LA according to ASTM D638. The measurements were conducted at room temperature (25°C). The cross-head speed was 5 mm/min. At least three test specimens of every composition were tested. The impact strength of the composites was tested according to ASTM D256 standard. A FRANK Baldwin-Model-BLI pendulum Impact testing machine was used to measure the not-notched rectangular specimens (80  $\times$  10  $\times$  3.8  $\text{mm}^3$ ). At least three specimens were tested for each sample. The shore A hardness of each bioblend was measured with a FRANK testing machine according to DIN53505. Seven measurements were taken into account for each sample. The SEM micrographs were obtained with Hitachi S4160 cold field emission instrument on surface and fracture surface of samples in liquid  $\text{N}_2$ .

## RESULTS AND DISCUSSION

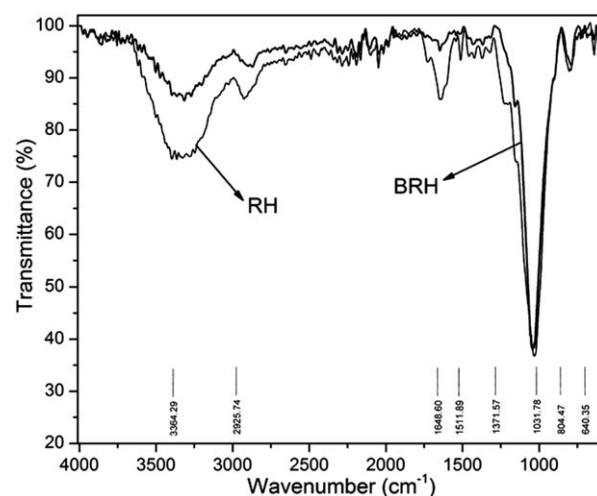
### FTIR Spectra

Figure 1 illustrates FTIR spectra of LASR3, LASR6, and LASR7. The peak at 1750  $\text{cm}^{-1}$  is assigned to the C=O stretching frequencies of PLLA or ester groups. The peak at 1182  $\text{cm}^{-1}$  is attributed to the C—O bond of PLLA. In addition, the peak at 1363  $\text{cm}^{-1}$  is indicative of the  $\text{CH}_3$  group of PLLA and also

**Figure 1.** FTIR spectra of LASR3, LASR6, and LASR7.

might represent the bending vibrations of starch CH groups. It is also seen that C—C peaks are appeared at 866  $\text{cm}^{-1}$ . The intensified peaks were appeared at 1129 and 1182  $\text{cm}^{-1}$  belong to C—OH and COC stretching of starch and cellulose content of RH. A peak was appeared at 2996  $\text{cm}^{-1}$  presents CH stretching vibrations of lignin which has been increased in LASR3 and LASR6; however, the amount is lower in LASR6. As is seen, a peak is appeared at 1587  $\text{cm}^{-1}$  in LASR3 which belongs to aromatic ring stretching band; however, this peak is much lower in LASR6 which is a proof of lignin removal.<sup>40–42</sup>

As shown in Figure 2, the peak at ca. 3364  $\text{cm}^{-1}$  indicates the existence of free hydroxyl groups; however, by bleaching it has been decreased. The peaks at ca. 2925, 1648, and 1511  $\text{cm}^{-1}$  indicates stretch of alkaline CH, lignin aromatic C=O, and C=C groups, respectively. A peak at 1371  $\text{cm}^{-1}$  may be attributed to the aromatic CH and carboxyl carbonate structures which in LASR6 has a tangible decrease. Finally, the peaks at 1031 and 804  $\text{cm}^{-1}$  belongs to Si—O—Si stretching and Si—H groups, respectively. It should be mentioned that the presence of polar groups on the surface can provide the considerable

**Figure 2.** FTIR spectra of RH and BRH.

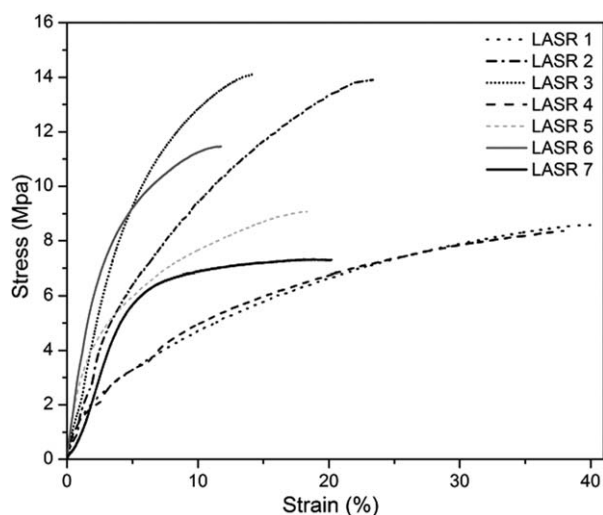


Figure 3. Stress–strain curves of samples.

cation exchange capacity.<sup>43</sup> As can be seen, by bleaching lignin, some peaks were disappeared.

#### Tensile Test

Tensile properties such as tensile strength, elongation at break, and Young modulus of the composites made from lignocelluloses fillers (RH and BRH), PLLA/starch blends at different filler loadings are shown in Figure 3 and Table II. The RH–PLLA–starch composites have shown higher strength compared to the BRH–PLLA–starch composites. As the bleaching process removed the lignin content in the RH, therefore, one may conclude that lack of lignin in the BRH is the main reason for the observed behavior.<sup>41</sup> The tensile strength of RH–PLLA–starch composites is slightly increased by increasing the filler loading (RH) and similar trend, that is, enhancement of tensile strength on filler loading, can be seen in the case of adding BRH filler.

The interesting point to be noticed here is that with increase in the content of BRH the extent of enhancement of tensile strength is slightly lower which proves that the removal of lignin could reduce the tensile strength and this matter will be proved by SEM results which will be described further. Conversely, RH leads to higher elongation at break as compared to the samples filled by BRH. Furthermore, elongation at break of samples,

decreased by increasing of filler content. It shows that introduction of fillers has made the composites more brittle and this could be due to the direct effect of silica which has been intensified by lignin removal.<sup>41,44</sup> It has been reported that high content of RH increases the probability of agglomeration, which results in regions of stress concentration requiring less energy for crack propagation.<sup>45</sup> The results show that the tensile strength of BRH samples increases by increasing the filler. However, at 15% of filler content, a reduction in tensile strength was observed. The elongation at break also demonstrates that removing the lignin in higher content of the filler has a negative effect on the properties. As is shown in Table II, elastic modulus (E-Modulus) of RH samples exhibit an increasing trend with increasing RH and BRH. During tensile loading, partially separated microspaces are created, which obstruct the stress propagation between the filler and the matrix. As both modified and unmodified filler loading increase, the degree of obstruction increases, which in turn, increases the modulus and stiffness.<sup>46</sup> The results further show the RH and BRH unplastification property.<sup>47</sup>

#### Charpy Impact

Based on the data obtained in Table II, the charpy impact strength shows a different behavior based on the type of the fillers. The charpy impact of RH-filled samples is decreased on an increase in filler content.

Eventually, the high loading of RH weakens the bonding between RH and matrix and reduces the impact strength. The result suggests that the RH is capable of absorbing energy due to the strong interfacial bonding with matrix<sup>46</sup> and the presence of lignin with plasticizing effect in RH-filled samples. On the contrary, there is an opposite trend for BRH-filled samples, in which the charpy impact is increased with an increase in filler content. The highest value of charpy impact strength is for the LASR6 (45.81 kJ/m<sup>2</sup>), which contains 15% BRH. Another interesting point is the larger amount of charpy impact strength for LASR6 compared to that of LASR3 which has the same content of RH. The reason for the different behavior of BRH- and RH-filled samples is related to the lignin removal of BRH samples which are unplastified.<sup>41,47</sup>

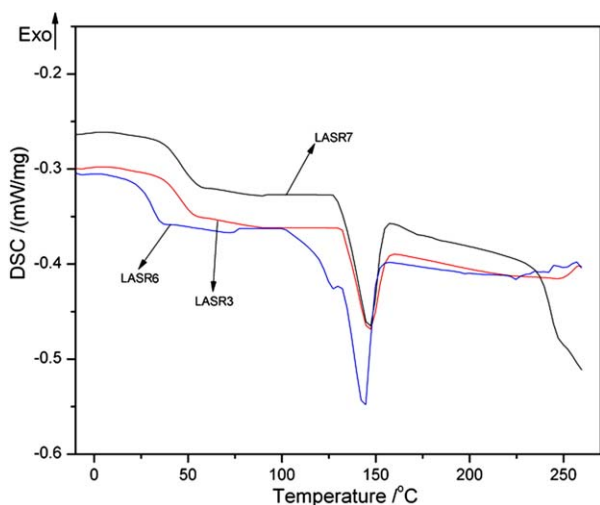
#### Shore A Hardness Test

The hardness of samples measured by shore A durometer is shown in Table II. It is evident that the hardness of samples is

Table II. Mechanical Properties of RH- and BRH-Filled Samples

Sample	Tensile strength (MPa)	Elongation at break (%)	Elastic modulus (MPa)	Charpy impact strength (kJ/m <sup>2</sup> )	Shore A hardness
LASR1	8.58	39.98	62.1	35.23	70.27
LASR2	13.89	23.38	159.77	24.15	71.41
LASR3	14.58	14.23	225.83	22.31	74.74
LASR4	8.36	37.92	205.85	38.01	70.7
LASR5	9.07	18.3	280.16	42.94	71.91
LASR6	11.46	11.75	303.18	45.81	74.92
LASR7	7.93	20.33	47.64	36.39	66.66

Standard deviation  $n = 5$ .



**Figure 4.** The crystallization exotherms of samples for nonisothermal crystallization from melt at a cooling rate of 10°C/min. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

increased on increment of the filler in composites. This could be attributed to both dispersion of the RH into the matrix with minimization of voids and stronger interfacial bonding between the RH and matrix.<sup>46,48</sup> Furthermore, the BRH samples exhibit higher hardness values than RH composites. This behavior may also be related to removal of lignin in the bleached samples.<sup>47</sup> For instance, LASR1 with 5% of RH and PLLA–starch sample (LASR7) show hardness values of 70 and 66, respectively. Therefore, it can be concluded that the filler improves the hardness of composites by filling the empty spaces between the polymer chains for both RH- and BRH-filled samples.

In general, the mechanical properties reveal that the range of 5–10% content of BRH or RH can be used as fillers leading to an improvement in the tensile properties as well as hardness. Furthermore, since the toxic lignin<sup>33</sup> was removed from the RH (BRH), it can be widely used in the food industry as safe and useful filler.

### DSC Thermograms

To investigate the effect of various loadings of RH and bleaching on the thermal behavior of starch–PLLA, DSC measurements were carried out. As most of the processing methods occur under nonisothermal conditions, the understanding of

**Table III.**  $T_m$ ,  $X_c$ ,  $\Delta H_c$ , and Width of Half Height Crystallization Peak of Samples

Samples	LASR3	LASR6	LASR7
$T_g$ (°C)	46.9	31.1	47
$T_m$ (°C)	143.8	147.5	146.4
$\Delta H_c$ (J/g)	5.804	13.98	8.473
WHH (°C)	11.4	10.9	11.9
$X_t^a$ (%)	6.24	15.03	9.11

<sup>a</sup>By considering the melting enthalpy of 100% crystalline poly(L-lactide) as 93 J/g.<sup>50</sup>

polymer crystallization under dynamic condition is of considerable importance.<sup>49</sup> The crystallization exotherms of blends are presented in Figure 4. The characteristic parameters of nonisothermal crystallization exotherms, such as the crystallization peak ( $T_m$ ), the relative degree of crystallinity ( $X_t$ ), in terms of  $\Delta H_c$  ( $H_c$  is the enthalpy of crystallization), and width of half height of crystallization peaks (WHH) are reported in Table III.

It can be observed that the normal RH has a negative effect on the crystallization peak as it reduces the temperature of crystallization. As expected, it also reduced the enthalpy of crystallization. LASR3 showed the lowest degree of crystallization among the other samples. Lignin significantly reduces the mobility of polymer chains because of their steric hindrance effect which ascribed to its crosslinked aromatic structure, addition of RH decreased the extent of crystallinity.

The most important point here is that the BRH-filled sample shows an increase in the crystallization peak and also a small second peak at 126°C. The other important effect of bleaching is that  $\Delta H_c$  is increased and as a result the relative crystallinity<sup>50</sup> has a slight increase. As is reported,<sup>51</sup> the RH is heavily used as a natural resource to produce silica and nanosilica particles, thus after the extraction of lignin through the bleaching process, the silica particles may become more active playing the role of nucleating agent leading to a higher degree of crystallization and give the blend hydrophobic properties in the case of LASR6.<sup>52</sup> The WHH data demonstrate that the crystallization will occur faster in LASR6 which contains BRH as filler.

Finally, the bleaching could shift the glass transition temperature to lower temperatures. As is reported,<sup>53</sup> PLLA has a  $T_g$  in the range of 60–65°C. It is observed that starch lowers  $T_g$  as it facilitates the mobility of chains. According to the results from DSC, the bleaching process could enhance the mobility of polymer chains due to removal of lignin which had a steric hindrance effect on the polymer chains leading to reduction of  $T_g$  in LASR6. We expect the addition of RH into the PLLA/starch (LASR7) would depress the mobility of polymer chains leading to a higher  $T_g$  but it can be observed that  $T_g$  exhibited no significant change for LASR3. We postulate that there could be an opposing effect. On one hand, as we expect, the presence of lignin could depress the mobility of polymer chains which might lead to larger  $T_g$ . Conversely, lignin can act as obstacle for mobility of the PLLA chains to fold and join the crystallization growth front, finally leading to a reduction in the extent of crystallinity. This reduction in degree of crystallization could result in lower amount of  $T_g$  due to effect on amorphous phase.<sup>49</sup> In conclusion, these two effects are the main dominating factors affecting the transition process and as could be seen these two effects counteract each other leading to no significant change in  $T_g$ .

### SEM Results

SEM technique was carried out to see the morphological difference of the samples on surface and fractured surface via LN<sub>2</sub>. According to Ludueña et al., their SEM pictures for RH, and the inner epidermis of RH have a smooth surface, while the outer surface is highly roughened and shows ridged structure. On bleaching and removal of lignin, the roughness was

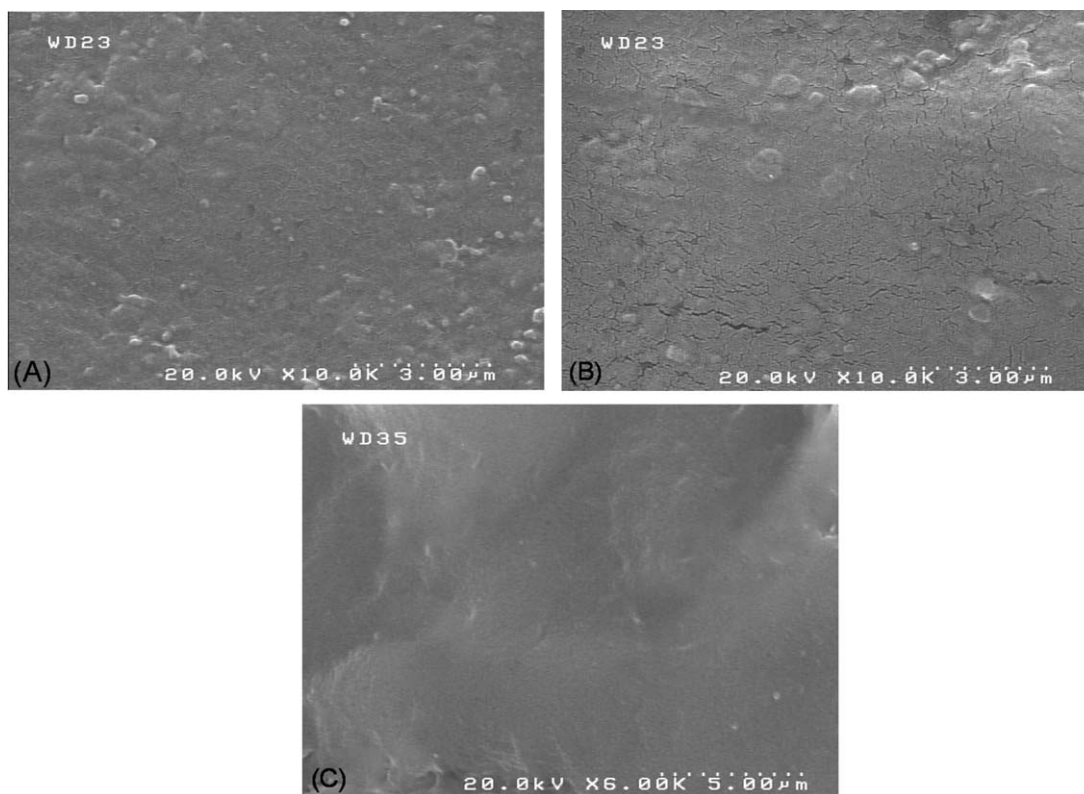


Figure 5. Surface of (A) LASR3, (B) LASR6, and (C) LASR7 acquired from SEM test.

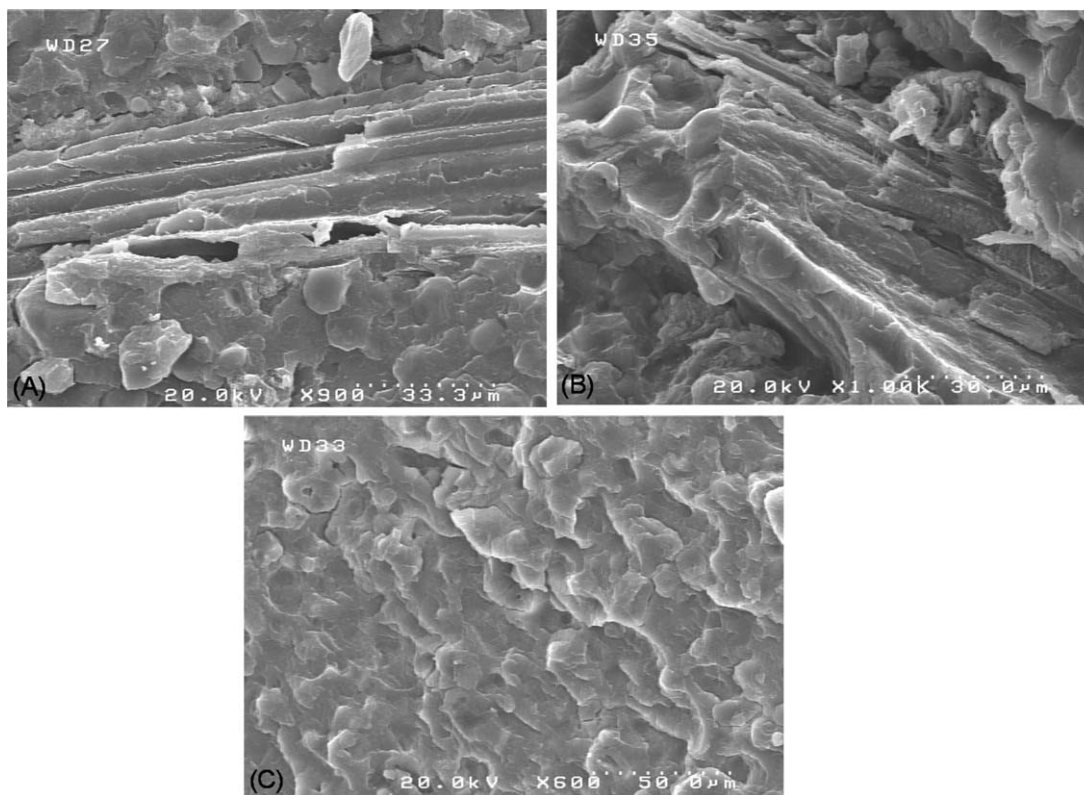


Figure 6. SEM pictures of the fracture surface of (A) LASR3, (B) LASR6, and (C) LASR7.

increased. The silica is mainly localized on the outer surface of RH and the high silica content on outer epidermis provides strength and stiffness to the husk.<sup>45</sup> As is approved by FTIR results, the content of silica has not changed which means the only effect is the removal of lignin. As is seen in Figure 5, the surface of sample without RH is quite consistent. On introduction of RH in samples, very small cracks are appeared. On removal of lignin in the BRH samples, these cracks are quite tangible which endorses the reported unplasticating effect. Figure 6 depicts the effect of RH on the fracture behavior of samples. As previously described, introduction of RH has made the composites more brittle and on removing the lignin this brittleness is increased on adding 15% of BRH. The brittle behavior shows that negative effect is observed when 10% filler is used. The results of mechanical properties such as tensile, charpy, and hardness are clarified with the SEM pictures. As can be seen in Figure 6(B), by removing lignin, the adhesion of RH to the matrix phase is increased.

## CONCLUSIONS

The results show that the filler content in PLA–starch blends could improve the mechanical properties of samples. Filler improved the tensile strength and hardness of blends. The charpy impact strengths of RH samples are lower than those without RH related to the plasticization role of lignin within RH. The mechanical properties reveal that 5–10% of BRH or RH may be used in composite which result in improvement of the tensile properties as well as hardness. Generally, by adjusting the blend composition and removing the lignin from RH, the mechanical properties were improved. Moreover, due to the presence of silica in RH, the crystallinity was also enhanced. The toxic lignin removal from the RH (BRH) could make it suitable for application in food industry as filler and the blend can be used as an alternative for food packaging, biodegradable food plates, and containers.

## REFERENCES

1. Tokiwa, Y.; Suzuki, T. *Nature* **1977**, *270*, 76.
2. Chiellini, E.; Solaro, R. *Adv. Mater.* **1996**, *8*, 305.
3. Koenig, M. F.; Huang, S. J. *Polymer* **1995**, *36*, 1877.
4. Ching, C. T. K.; Kaplan, D. L.; Thomas, E. L. *Biodegradable Polymers and Packaging*; Technomic Publisher: Lancaster, **1993**, p 151.
5. Vaidya, U. R.; Bhattacharya, M. *J. Appl. Polym. Sci.* **1994**, *52*, 617.
6. Lee, S. H.; Lee, K. H.; Hong, S. K. *J. Appl. Polym. Sci.* **1997**, *64*, 1999.
7. Kweon, D.-K.; Lim, S.-T. *J. Appl. Polym. Sci.* **2001**, *81*, 2197.
8. Kweon, D.-K.; Cha, D.-S.; Park, H.-J.; Lim, S.-T. *J. Appl. Polym. Sci.* **2000**, *78*, 986.
9. Dubois, P.; Krishnan, M.; Narayan, R. *Polymer* **1999**, *40*, 3091.
10. Cho, C. G.; Lee, K. *Carbohydr. Polym.* **2002**, *48*, 125.
11. Pomeranz, Y. *Wheat is Unique: Structure, Composition, Processing, End-Use Properties, and Products*; American Association of Cereal Chemists, St Paul, Minnesota, **1989**, 277–302.
12. Eliasson, A.-C. *Carbohydrates in Food*, 2nd ed.; Taylor & Francis: New York, **2006**, p 431–503.
13. Averous, L.; Moro, L.; Dole, P.; Fringant, C. *Polymer* **2000**, *41*, 4157.
14. Sarazin, P.; Li, G.; Orts, W. J.; Favis, B. D. *Polymer* **2008**, *49*, 599.
15. Dos Santos Rosa, D.; EduardoVolponi, J.; Fassina Guedes, C.; Das, G. J. *Appl. Polym. Sci.* **2006**, *102*, 825.
16. Spěváček, J.; Brus, J.; Divers, T.; Grohens, Y. *Eur. Polym. J.* **2007**, *43*, 1866.
17. Xiong, Z.; Yang, Y.; Feng, J.; Zhang, X.; Zhang, C.; Tang, Z.; Zhu, J. *Carbohydr. Polym.* **2013**, *92*, 810.
18. Chen, L.; Qiu, X.; Deng, M.; Hong, Z.; Luo, R.; Chen, X.; Jing, X. *Polymer* **2005**, *46*, 5723.
19. Park, J. W.; Im, S. S.; Kim, S. H.; Kim, Y. H. *Polym. Eng. Sci.* **2000**, *40*, 2539.
20. Park, J. W.; Lee, D. J.; Yoo, E. S.; Im, S. S.; Kim, S. H.; Kim, Y. H. *Korea Polym. J.* **1999**, *7*, 93.
21. Gao, H.; Hu, S.; Su, F.; Zhang, J.; Tang, G. *Polym. Compos.* **2011**, *32*, 2093.
22. Arvanitoyannis, I.; Biliaderis, C. G.; Ogawa, H.; Kawasaki, N. *Carbohydr. Polym.* **1998**, *36*, 89.
23. Bagley, E. B.; Fanta, G. F.; Burr, R. C.; Doane, W. M.; Russell, C. R. *Polym. Eng. Sci.* **1977**, *17*, 311.
24. Griffin, G. J. L. *Chemistry and Technology of Biodegradable Polymers*; Chapman & Hall: London, **1994**, p 18–47.
25. Griffin, G. J. L. *Polym. Degrad. Stab.* **1994**, *45*, 241.
26. Patil, D. R.; Fanta, G. F. *starch-starke* **1994**, *46*, 142.
27. St-Pierre, N.; Favis, B. D.; Ramsay, B. A.; Ramsay, J. A.; Verhoogt, H. *Polymer* **1997**, *38*, 647.
28. Yew, G. H.; Mohd Yusof, A. M.; Mohd Ishak, Z. A.; Ishiaku, U. S. *Polym. Degrad. Stab.* **2005**, *90*, 488.
29. Yang, H.-S.; Kim, H.-J.; Son, J.; Park, H.-J.; Lee, B.-J.; Hwang, T.-S. *Compos. Struct.* **2004**, *63*, 305.
30. Razavi-Nouri, M.; Jafarzadeh-Dogouri, F.; Oromiehie, A.; Langroudi, A. E. *Iran. Polym. J.* **2006**, *15*, 757.
31. Sakagami, H.; Asano, K.; Yoshida, T.; Kawazoe, Y. *In Vivo* **1999**, *13*, 41.
32. Malherbe, S.; Cloete, T. E. *Rev. Environ. Sci. Biotechnol.* **2002**, *1*, 105.
33. Khanam, L. M.; Talukder, D.; Hye, M. A. *Univ. J. Zool. Rajshahi Univ.* **2006**, *25*, 27.
34. Gilding, D. K.; Reed, A. M. *Polymer* **1979**, *20*, 1459.
35. Davachi, S. M.; Kaffashi, B.; Roushandeh, J. M. *Polym. Adv. Technol.* **2012**, *23*, 565.
36. Mohammadi-Rovshandeh, J. *Cellul. Chem. Technol.* **2005**, *39*, 73.
37. Wise, L. B.; D'Addieio, A. A.; Murphy, M. *Pap. Trade J.* **1946**, *122*, 35.

38. Yildiz, S.; Gezer, E. D.; Yildiz, U. C. *Build. Environ.* **2006**, *41*, 1762.
39. Hwang, S. W.; Shim, J. K.; Selke, S.; Soto-Valdez, H.; Rubino, M.; Auras, R. *Macromol. Mater. Eng.* **2013**, *298*, 624.
40. García, N. L.; Lamanna, M.; D'Accorso, N.; Dufresne, A.; Aranguren, M.; Goyanes, S. *Polym. Degrad. Stab.* **2012**, *97*, 2021.
41. Chen, L.; Qiu, X.; Xie, Z.; Hong, Z.; Sun, J.; Chen, X.; Jing, X. *Carbohydr. Polym.* **2006**, *65*, 75.
42. Lisperguer, J.; Perez, P.; Urizar, S. *J. Chil. Chem. Soc.* **2009**, *54*, 460.
43. Daffalla, S. B.; Mukhtar, H.; Shaharun, M. S. *J. Appl. Sci.* **2010**, *10*, 1060.
44. Ludueña, L.; Fasce, D.; Alvarez, V. A.; Stefani, P. M. *BioResources* **2011**, *6*, 1440.
45. Karmarkar, A.; Chauhan, S. S.; Modak, J. M.; Chanda, M. *Compos. A: Appl. Sci. Manuf.* **2007**, *38*, 227.
46. Rahman, M. R.; Islam, M. N.; Huque, M. M.; Hamdan, S.; Ahmed, A. S. *BioResources* **2010**, *5*, 854.
47. Kamoun, A.; Jelidi, A.; Chaabouni, M. *Cem. Concr. Res.* **2003**, *33*, 995.
48. Rahman, M. R.; Huque, M. M.; Islam, M. N.; Hasan, M. *Compos. A: Appl. Sci. Manuf.* **2008**, *39*, 1739.
49. Seyfi, J.; Hejazi, I.; Mohamad Sadeghi, G. M.; Davachi, S. M.; Ghanbar, S. *J. Appl. Polym. Sci.* **2012**, *123*, 2492.
50. Torabinejad, B.; Mohammadi-Rovshandeh, J.; Davachi, S. M.; Zamanian, A. *Mater. Sci. Eng. C* **2014**, *42*, 199.
51. Noushad, M.; Rahman, I. A.; Husein, A.; Mohamad, D.; Ismail, A. R. *Int. J. Adv. Sci. Eng. Inf. Technol.* **2012**, *2*, 28.
52. Srisawat, N.; Nithithanakul, M.; Srikulkit, K. *J. Met. Mater. Miner.* **2009**, *19*, 53.
53. Ray, S. S.; Okamoto, M. *Macromol. Rapid Commun.* **2003**, *24*, 815.