Preparation of Rice Husk-Based Medium Density Fiberboards: Effects of pH Modification on Mechanical and Tribological Performance

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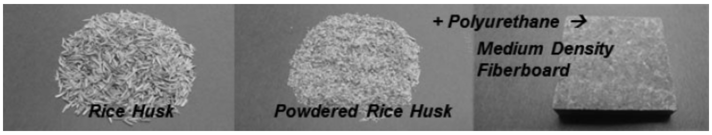
Rice husk (RH) is a major waste byproduct of global rice paddy production. Powdered RH is mixed with a polymeric resin to produce RH-based medium density board. Resin concentration is varied and several particles sizes of RH powder are tested. The RH powder is subjected to acidic, neutral, and alkaline treatments to determine how they affect adhesion of the resin to the powder. The adhesion controls, to a large extent, the mechanical and tribological performance. Thus, mechanical and tribological properties of fiberboards prepared from untreated RH powder are compared to treated specimens and the effects of pH are determined. The mechanical performance of the RH-based MDF compares favorably to similar commercial building materials.



1. Introduction

The rice crop constitutes a significant part of global cereal grain production; for instance, in 2008 the world rice paddy production was 661 million tons.[1] Rice husk (RH) represents a high percentage of the dried paddy on-stalk: 20% is husk, 52% corresponds to white rice, 15% is stalk, and 10% is bran. Thus, along with edible rice, some 132 million tons of RH were also produced in 2008. Rice husk ash (RHA) – comprised of 85% or more silica – is obtained from burning the rice husk (RH). Malaysia alone reportedly produces more than 81 000 metric tons of RHA annually,[2] and the RHA can then be utilized, for example, in construction materials,[3] as catalysts and catalyst supports,[4] or for remediation of pollution by SO_2 emissions.[2] RH itself is a fibrous material with poor nutritional properties, low bulk density, low digestibility, high silica content, and high abrasion properties, i.e., it is by itself an abrasive material.

RH is usually still considered a waste material. Owing to the expense and difficulty of transporting it, it is often burned in the open or dumped on wasteland. The most practical use of RH is consequently as fuel at or close to the rice mill (though with low caloric content). Nevertheless, RH is considered as a commodity[5–7] for a few non-energy applications, while its low density and low flammability actually render it a good insulator. Thus RH is used in low proportion in several low-value applications such as: metal absorption,[8–10] filler in construction materials (especially

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concrete) to reduce density,[11–14] polymer reinforcement,[15–21] roughage for ruminants, additives to improve soil quality, litter material for pet animals, and hydroponics. Its high silica content (up to 22% by weight) makes RH inappropriate for human or animal consumption; the total digestible nutrient content of RH is $<10\%$,[22–25] while starch is practically absent. In fact, RH is considered a harmful agro-industrial waste: proper disposal is needed to mitigate potential problems of environmental pollution (by silicosis). These harmful effects and low digestibility and nutritional value are due to the high mineral content.

Previous studies have shown that RH has its outer surface formed by long rectangular to elliptical cells with waxy walls arranged in axial rows with simple, thick-walled hairs randomly distributed; the lateral walls of the cells are highly wavy or toothed so that adjacent cells fit snugly together, while the external surface has been described as composed of dentate rectangular elements.[5–7] This particular morphology provides the RH with interesting abrasive properties. The inner surface of the husk is relatively smooth and free of hairs. One important aspect of this peculiar morphology is that silica is highly concentrated in the outer surface of the husk producing a material with high hardness (between 5.5 and 6.5 in the Mohs scale) and with the important property of flame retardancy. For these reasons, one of the most recent and important applications is fabrication of agglomerates or medium density fiberboards (MDFs) that are flame-retardant.[15–19] Furthermore, the dentate morphology of RH provides a means to tailor the tribological properties of the MDF surface. Such a RH-based MDF is comprised of powdered RH blended with a polymeric resin as agglutinant agent. Since MDF is widely used and durable as a construction material, the effective design of RH-based MDF – not requiring wood products – has potential to yield more sustainable MDF.

To prepare a polymer resin + RH fiberboard, the lignin must first be removed from the husk since lignin is present at high concentration (up to 20 wt%) and limits accessibility and adhesion between the polymer resin and the cellulosic component of the RH. In the case of a polyurethane (PU) MDF, the essential chemical reaction occurs between the cellulose primary hydroxyl (in RH) and the cyano groups present in the PU resin–polyisocyanate mixture. Lignin removal can be achieved by various chemical treatments.[26–29] For example, attack by sodium hydroxide removes surface lignin and frees the hemicellulose for reactivity with the PU constituents to produce a crosslinking between all of the MDF's constituents.

Thus, attaining good chemical reactivity and adhesion between components is key to preparing MDF from RH. We therefore tested several chemical treatments intended to improve adhesion between the RH and the polymer resin. Various properties of the prepared materials were evaluated to assess performance of the RH-based fiberboards. The RH was first ground to a powder and chemically treated at different pH: 1, 4, 7, 10, and 12. The impact of chemical treatment on the mechanical and tribological properties is discussed. Additionally, resin concentrations and husk particle size were varied to determine their roles in the properties of the final products.

2. Experimental Section

2.1. Rice Husk Treatments

Dried RH, obtained from IPACPA, Cordoba, Veracruz, Mexico, was ground in a Pulvex model P-300 mill. Three different particle sizes were obtained: 150 (small S), 425 (medium M), and 900 (large L) microns. A fraction of each of these powders was immersed, at room temperature, in water at five different pH: 1 and 4 using HNO_3, 10 and 12 using NH_4OH, and 7 using plain faucet water with a confirmed neutral pH. In all cases, the immersion time was 120 min. After this treatment, the powders were rinsed with plain water to remove the acid or base excess. The rinsed powder was spread on a horizontal flat surface for drying at room temperature until a constant weight was reached. An untreated fraction of each powder was used as a reference for comparison purposes: these powders were not immersed in any liquid and are designated as ''Ref.''

2.2. MDF Fabrication

The fiberboards were prepared using solvent free alkyd PU as the agglutinating agent: an alkyd hydroxylated resin (Reichhold, Mexico) was catalyzed with polyisocyanate (Bayer, Germany) in a ratio 4:1. Once the hydroxylated resin was mixed with the polyisocyanate, the mixture was added slowly to the dry RH powder and mixed manually to obtain uniform dough. Samples at three different resin concentrations, with respect to RH, were prepared: 15, 17.5, and 20% by weight. Also powders of three different sizes (S, M, and L), each treated at different pH (1, 4, 7, 10, 12, and Ref) were used in the sample preparation.

Medium density fiberboards were prepared according to the norm ASTM D 790-92: once the resin and the RH were perfectly mixed, the RH powders impregnated with the resin were placed in an aluminum mold of 6.4 mm × 13 mm × 130 mm and compacted at a pressure of ≈3 000 psi (21 MPa) at 120 °C during 15 min. At the end of this time, the heat source was turned off while the pressure was maintained. Once the boards cooled down to 40 °C, they were removed from the mold. In this way, it was possible to obtain fiberboards with the right density while the chemical reaction, accelerated by the high temperature, provided the boards with the appropriate dimensional stability. The prepared specimens were allowed to rest for 24 h prior to testing.

2.3. Mechanical Tests

The mechanical tests were performed according to the norm ASTM D-695-02a in an Adamel Lhomargy machine model DY.22 in compression mode with a compression rate of (1.3 ± 0.3) mm min^{-1}. The cell load was 5 000 N with a resolution of 0.1 N; five probes were prepared for each composition, and the average values of the Young modulus and force to rupture are reported.

2.4. Tribological Tests

The abrasion behavior was evaluated according to the norm ASTM-D-1242-95 (Taber method) by measuring the weight lost as a function of the wearing time; values were collected every 20 s. Dynamic friction of the prepared MDF specimens was determined on a Nanovea Pin-on-disk Tribometer. Samples were tested at room temperature using a 2 mm steel ball at 200 rpm for 4 000 revolutions. Samples were tested at loads of 10 and 15 N.

2.5. Water Absorption Tests

Water absorption by the MDF was evaluated according to the norm ASTM D 570-98. Small disks of 50.8 mm diameter and 3.2 mm thickness were completely immersed in closed bottles filled with distilled water. Two different immersion times were chosen: 120 and 1 440 min (24 h). The samples were weighed before and after immersion, ensuring the removal of excess water from the surface.

3. Results and Discussion

The chemical treatment of RH powders, in acidic or alkaline conditions, modifies the RH surface to provide better interactions with the polymeric resin and thereby improved adhesion. This treatment improves the accessibility of the cyano group to the primary hydroxyls of the cellulose once the lignin has been removed. Independent of the acid or basic treatment, the reaction between the primary hydroxyl of the cellulose [(Cel)-OH] and the polyisocyanate (OCN-R-NCO) can be schematically written as:

$$2[(\text{Ce1}) - \text{OH}] + \text{OCN} - \text{R} - \text{NCO} \rightarrow (\text{Cel}) - \text{O} - \text{CO} - \text{NH} - \text{R} - \text{NH} - \text{CO} - \text{O} - (\text{Cel})$$

It can be seen that the polyisocyanate produces a crosslinking effect between RH particles, yielding a positive effect on the mechanical performance of the fiberboards.

Figure 1 shows the Young modulus Y for all samples prepared at different pH and with different particle sizes. On the left of the horizontal axis are reported the samples with untreated RH powders (Ref). In some cases, acid treatment may produce an increase in Y with respect to the reference specimens: the highest Young modulus values were obtained for samples with 20% resin and for small and medium particle sizes. However, at lower resin content (17.5% or less), the untreated reference samples displayed the best results.

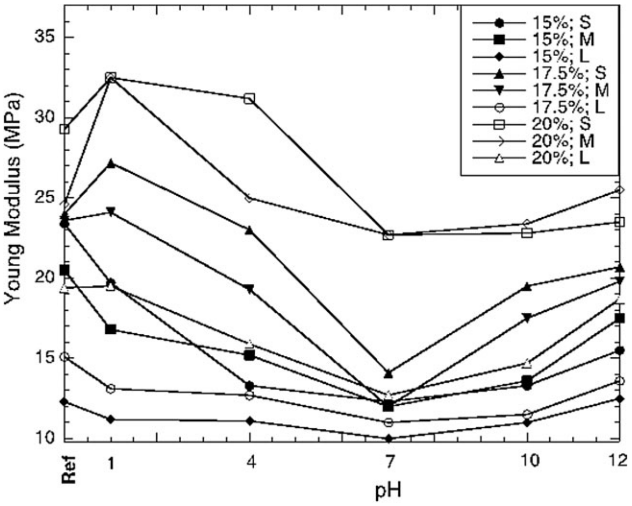

Figure 1. Young modulus of the rice husk-based MDF's as a function of the pH of chemical treatment. Data on the left hand side of the horizontal axis indicated with "Ref" corresponds to samples prepared without any chemical treatment. The legend indicates resin concentration (as a percentage) and husk powder size (S, M, and L).

Alkaline treatments (pH 10 or 12) yielded Young moduli similar to those reported for the reference samples. There was not significant improvement in the mechanical properties when the RH powders were alkaline treated; thus, in this regard, it is better to incorporate the RH powder with no prior treatment.

All samples prepared with powder immersed in plain water (pH 7) had the lowest Young modulus. This behavior is due in part to limited reactivity of RH —OH groups with cyano groups of the resin since immersion of the RH powder in water does not remove the lignin coating that partially masks the primary hydroxyls. However, it seems that the most important factor for the reduction in the Young modulus is the moisture (traces of water) that are kept trapped in the pores of the RH and that are difficult to remove completely. These very small amounts of water react with the cyano groups blocking the reaction with the primary hydroxyl of the cellulose; for this reason the mechanical properties are reduced. Because it is important to obtain fiberboards with good mechanical properties, it is essential to use dry RH powder: immersion of husk powder in plain water results in extensive water absorption, which prevents adhesion between the RH and the resin.

Figure 2 provides the force to rupture F_R, i.e., the yield strength, as a function of pH. As with the Young modulus, an increase in F_R, with respect to reference samples, was attained for samples with pH 4 and high resin content. As before, for pH between 7 and 10, there was a significant reduction in F_R; the reasons for this behavior are the same

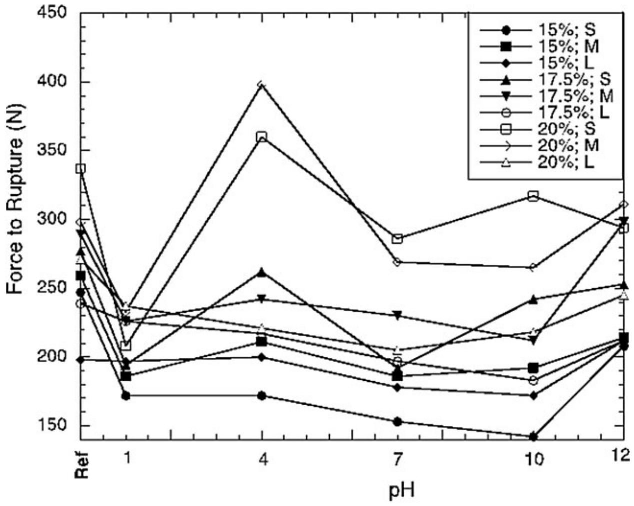

Figure 2. Force to rupture of the rice husk-based MDF's as a function of the pH of chemical treatment. Data on the left hand side of the horizontal axis indicated with "Ref" corresponds to samples prepared without any chemical treatment. The legend indicates resin concentration (as a percentage) and husk powder size (S, M, and L).

as mentioned in the former case. Generally, for all particle sizes and concentrations, good values for the force to rupture were obtained from using the RH powder treated with acid or without any treatment. Beyond that, results for specimens with small particle size were typically best.

Figure 3 provides a comparison of Young modulus and force to rupture of RH-based MDF, triply (a three-ply wood construction material), and wood agglomerate (construction material consisting of wood powder and resin, similar to but not the same as MDF). In Figure 3a, the Young modulus is reported for wood agglomerate, triply, and RH boards (at three different resin concentrations, with the small RH particle size (150 μm) after treatment at pH 4 or no-treatment, i.e., Ref). As can be noticed, triply has the highest Young modulus; this is due to its structure: the wooden plates that form the triply are oriented in perpendicular directions to each other, which improves the mechanical properties in all directions. The two materials with the next highest Young modulus values are RH-based MDF with 20% resin and with powder treated at pH 4 or with the Reference powder. In the ensuing discussion, RH based MDF samples are denoted by the material identifier (RH, i.e., RH based MDF), resin concentration (% R), particle size (S, M, and L), and chemical treatment (pH value or Ref) in abbreviated notation.

It is interesting to note that three samples have practically the same Young modulus: the sample [RH 17.5% R, S, pH 4] with 23 MPa; the sample [RH 17.5% R, S, Ref] with 24 MPa; and the sample [RH 15% R, S, Ref] with 23.5 MPa, the last one being the sample with the lowest resin content. The sample [RH 20% R, S, pH 4], with a Young modulus of 31 MPa, appears to benefit from a higher resin concentration. The Young modulus for the wood agglomerate (20.5 MPa) is lower with respect to [RH 15% R, S, Ref]. Even the worst case, corresponding to [RH 15% R, pH 4], has a Young modulus of 13.3 MPa, which is not excessively lower than the highest value of 31 MPa. Therefore at low resin concentration, it is still possible to obtain a reasonable Young modulus in MDF with RH powder having an acid treatment or no-treatment at all.

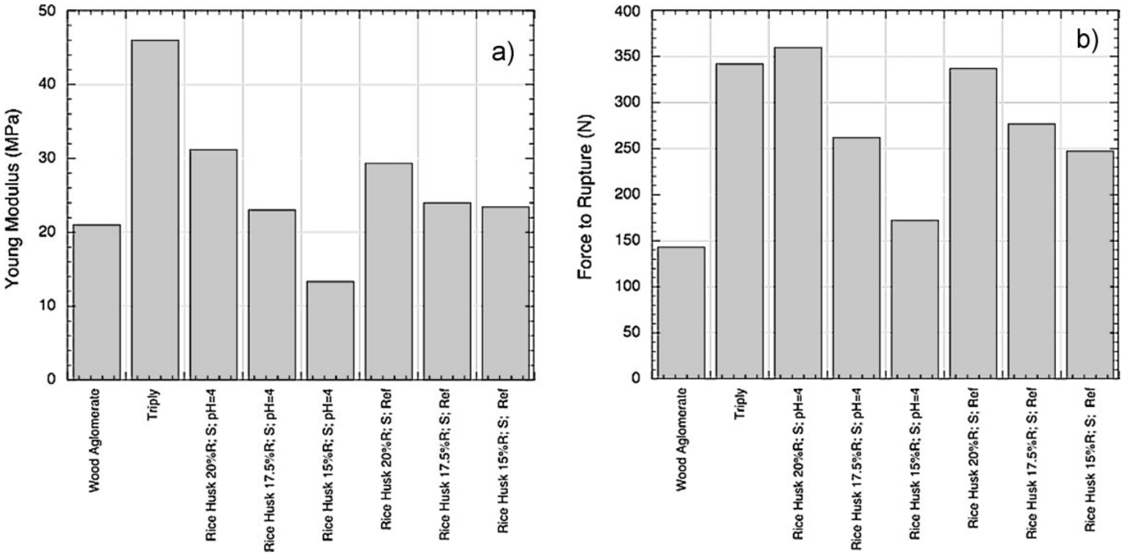

Figure 3. A comparison between different boards: triply, wood agglomerate and rice husk-based MDF's: a) Young modulus, b) force to rupture. The data for rice husk boards correspond to samples with different resin concentrations (shown as percentages) but all with small particle size (S). These samples include the Ref. specimens and those treated at pH of 4.

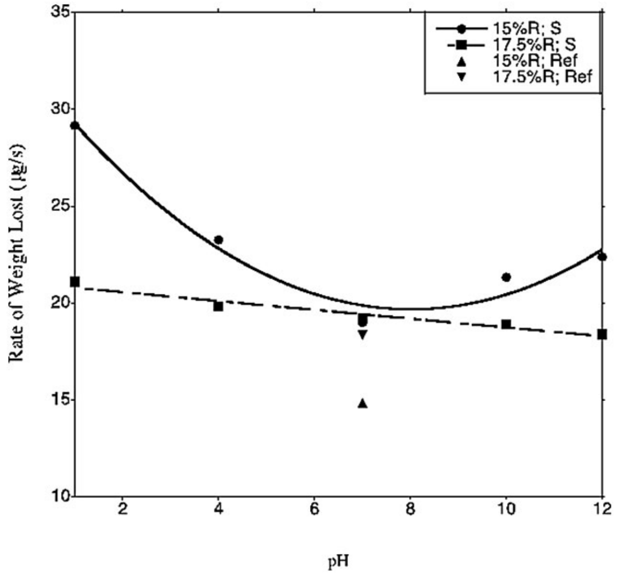

Figure 4. Abrasion results are shown as the rate of weight lost. Data points are for 15 and 17.5% resin concentrations containing small husk particle size. The pH of chemical treatment is shown along the *x*-axis, with reference samples included as points at pH 7.

Generally, the yield strength (F_R) values (Figure 3b) followed the same trend as those of the Young modulus (Figure 3a). F_R is practically the same for triply, for [RH 20% R, S, pH 4], and for [RH 20% R, S, Ref] (the values lying between 340 and 350 N). As before, for low resin concentrations, higher F_R values were obtained with the untreated powder.

Abrasion results are reported in Figure 4 for specimens prepared with the small particles (S) and low resin contents (15 and 17.5%); the weight loss rate for the other samples was significantly higher (more than 20%) than for the aforementioned samples and they were thus not included in the figure. The curve for 15% resin containing small particle size shows a minimum at pH 7; however, for samples with 17.5% R (including Ref), the abrasion resistance is practically independent of pH.

The water absorption of the prepared RH-MDF is reported in Figure 5 for two different immersion times: 120 and 1 440 min. The behavior for short and long absorption times is similar: overall water absorption is the least for samples containing the smallest RH particle size. For each series of samples prepared with the same powder size, water absorption was minimized at 17.5% resin concentration. This may be reflective of increased absorption due to the —OH groups present at high concentration in the resin and the possibility that some of the cyano groups did not react with the resin or the RH but with water molecules. Note however that for samples containing the small particle size, the system appears to reach saturation, with the water absorption being constant for 17.5 and 20% resin content (Figure 5b). Information about water absorption is important because dimensional stability and all mechanical and tribological properties depend on water absorption; furthermore, waterproof boards have a useful lifetime considerably longer than permeable boards.

Figure 6 shows the dynamic friction (at 10 N load) as a function of pH for all powder sizes and resin concentrations. There is a tendency toward higher static friction for larger particles. Such behavior is expected because, as mentioned in the Section 1, high silica content and toothed morphology of RH particles results in high

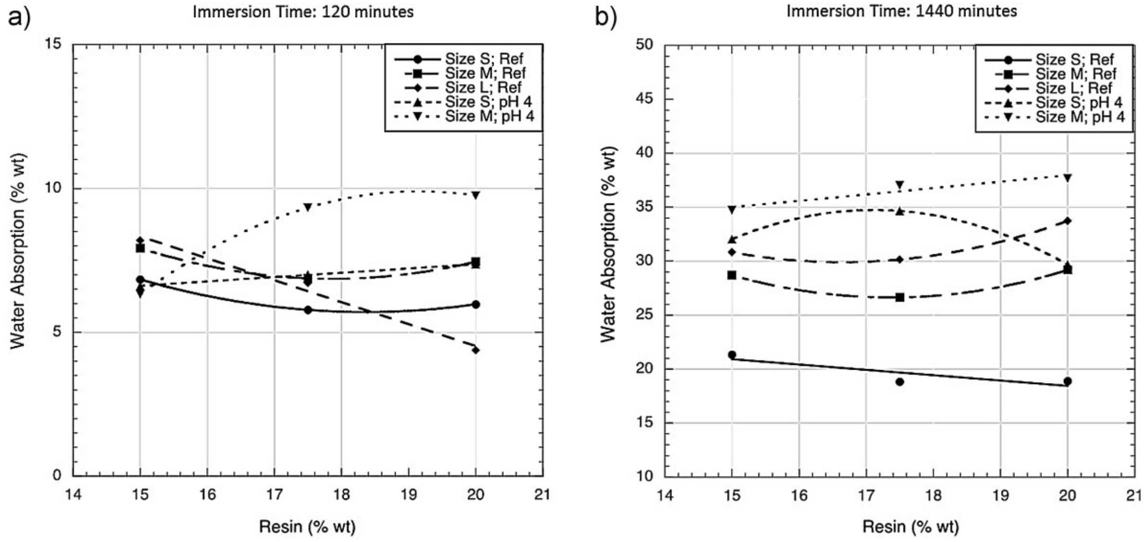

Figure 5. Water absorption by the MDF for: a) immersion time of 120 min, and b) immersion time of 1 440 min. Data shown for reference specimens and those treated at pH of 4.

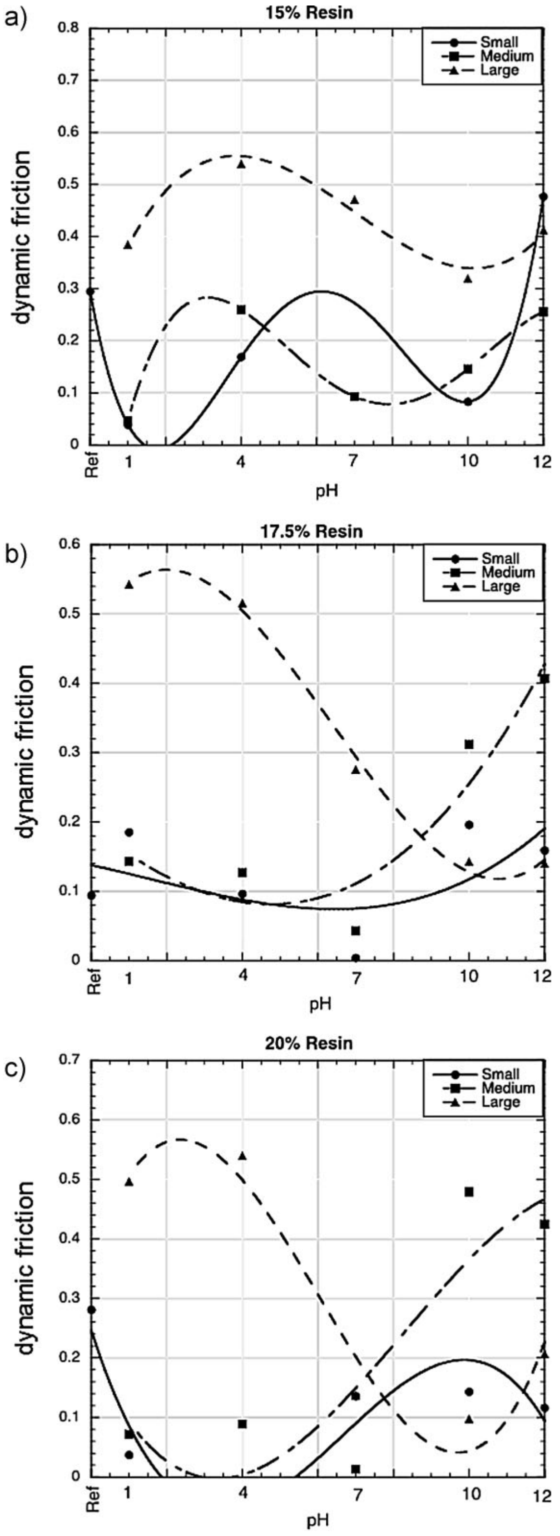

Figure 6. Dynamic friction values from testing at 10 N load, plotted versus the pH of chemical treatment. The rice husk-based MDF samples contain (a) 15% resin, (b) 17.5% resin, and (c) 20% resin, all with either small, medium, or large sized husk powder, as indicated.

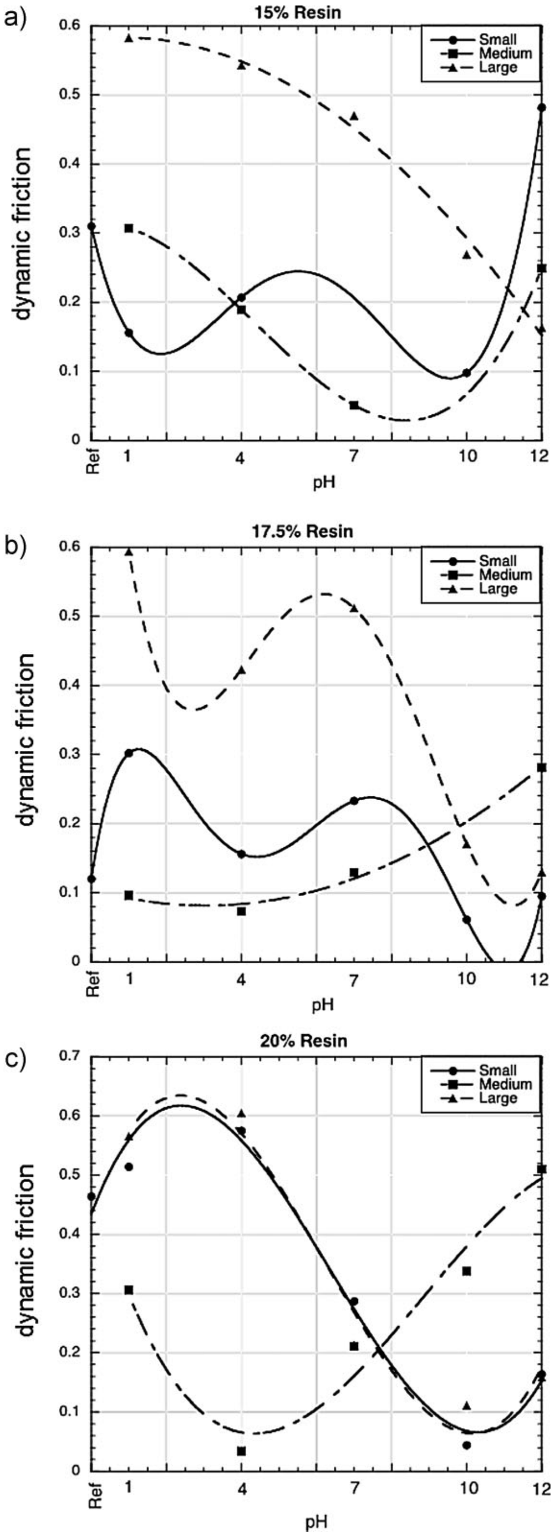

Figure 7. Dynamic friction values from testing at 15 N load, plotted versus the pH of chemical treatment. The rice husk-based MDF samples contain (a) 15% resin, (b) 17.5% resin, and (c) 20% resin, all with either small, medium, or large sized husk powder, as indicated.

friction. The effect on dynamic friction of resin content is small compared to the effect of particle size on the same property. The dynamic friction behavior at the higher load of 15 N, shown in Figure 7, is similar: large particles produce high dynamic friction.

4. Conclusions

In summary, while acid treatment can increase the Young modulus and yield strength for some samples, namely, those containing the largest amount of resin (20%), alkaline treatment yields behavior similar to that of the reference samples. Thus it is preferable to use RH powder as obtained or to treat it with acid. An advantage of the first scenario is that it eliminates the need for adding what would be a further cost in fiberboard fabrication. Compared to commercially available construction materials, mechanical properties of the rice-husk-based MDF were within range of those readily available options.

Moreover, the RH powder should be dry for effective reaction between the cyano groups of the resin binder and the cellulose primary hydroxyl of the RH. This reaction produces adhesion between phases, which improves mechanical performance. It is also possible for the resin to dissolve lignin present on the RH powder, thereby favoring the mentioned chemical reaction and also suggesting a further reason for observing the best mechanical performance at the highest resin content. Another reason for the good performance at high resin content is that the higher the amount of resin binder, the easier is the wetting of the RH powder. Small particles have high specific surface area and are harder to wet. There must be a minimum amount of resin required to ensure perfect wetting of the RH powder, and that amount should reasonably increase as the size of the particles decreases.

Rice husk particle size also played a part in determining the mechanical and tribological properties of the MDF. The best abrasion resistance was obtained for samples containing the smallest particle size, treated with acid or without treatment (Ref.). Young modulus and yield strength were likewise best for samples containing the small RH powder. A range of friction values were attained, with higher friction corresponding to large particle size and lower friction corresponding to small particle size. As it relates to wear, the tribological results are important since fiberboard is likely to suffer from continuous wear. Our results indicate that particle size and pH of chemical treatment can be adjusted to yield desired properties for a given application of the MDF. We plan to proceed with some further investigation on the preparation and properties of these materials, comparing them to other closely matched commercial materials and working to decrease their water absorption.

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[1] Milling: Rice husk, http://www.knowledgebank.irri.org/rkb/rice-milling/byproducts-and-their-utilization/rice-husk.html.
[2] I. Dahlan, K. T. Lee, A. H. Kamaruddin, A. R. Mohamed, *Environ. Sci. Technol.* **2008**, *42*, 1499.
[3] M. Cruz-Yusta, I. Mármol, J. Morales, L. Sánchez, *Environ. Sci. Technol.* **2011**, *45*, 6991.
[4] S. Wang, *Sci. Technol.* **2008**, *42*, 7055.
[5] B. S. Luh, (Ed.), *Rice, Vol. II: Utilization*, 2nd ed., Springer, Heidelberg **1991**.
[6] B. O. Juliano, in *Rice: Chemistry and Technology* (Ed., B. O. Juliano), Amer. Association of Cereal Chemists, St. Paul, MN, **1985**, p. 689.
[7] D. F. Houston, *Rice Chemistry and Technology*, American Association of Cereal Chemists, St. Paul, MN, **1972**, p. 301.
[8] M. J. Hu, Y.-L. Wei, Y.-W. Yang, J.-F. Lee, *J. Phys.: Condens. Matter* **2004**, *16*, S3473.
[9] D. P. Tiwari, D. K. Singh, D. N. Saksena, *J. Environ. Eng.* **1995**, *121*, 479.
[10] W. Nakbanpote, B. A. Goodman, P. Thiravetyan, *Colloids Surf. A: Physicochem. Eng. Aspects* **2007**, *304*, 7.
[11] V. Saraswathy, H.-W. Song, *Construct. Build. Mater.* **2007**, *21*, 1779.
[12] G. Graccio, G. Rodríguez de Cénsale, R. Zerbino, *Cement Concrete Compos.* **2007**, *29*, 566.
[13] G. C. Cordeiro, R. D. Toledo-Filho, L. M. Tavares, E. de Moraes-Rego, S. Hempel, *Cement Concrete Compos.* **2011**, *33*, 529.
[14] V. Ganvir, K. Das, *J. Hazard. Mater.* **2011**, *185*, 1287.
[15] B. S. Ndazi, S. Karlsson, J. V. Tesha, C. W. Nyahumwa, *Composites A* **2007**, *38*, 925.
[16] A. G. Facca, M. T. Kortschot, N. Yan, *Compos. Sci. Technol.* **2007**, *67*, 2454.
[17] O. Faruk, A. K. Bledzki, H.-P. Fink, M. Sain, *Prog. Polym. Sci.* **2012**, *37.11*, 1552. DOI 10.1016/j.progpolymsci.2012.04.003
[18] E. P. Ayswarya, K. F. Vidya Francis, V. S. Renju, E. T. Thachil, *Mater. Des.* **2012**, *41*, 1. DOI: http://dx.doi.org/10.1016/j.matdes.2012.04.035
[19] C.-S. Wu, *Polym. Degrad. Stabil.* **2012**, *97*, 64.
[20] B. Bilyeu, W. Brostow, L. Chudej, M. Estevez, H. E. Hagg Lobland, J. R. Rodriguez, S. Vargas, *Mater. Res. Innov.* **2007**, *11*, 181.
[21] M. Estevez, S. Vargas, A. de la Isla, W. Brostow, V. M. Castaño, J. R. Rodriguez, *Mater. Res. Innov.* **2005**, *9*, 61.
[22] S. Yoshida, Y. Ohnishi, K. Kitaishi, *Soil Sci. Plant Nutr.* **1962**, *8*, 15.
[23] J. James, M. Subba Rao, *Am. Ceram. Soc. Bull.* **1986**, *65*(8), 1177.
[24] R. V. Krishnarao, M. M. Godkhindi, M. Chakraborty, P. G. Mukunda, *J. Am. Ceram. Soc.* **1991**, *74*, 2869.
[25] R. V. Krishnarao, Y. R. Majan, T. J. Kumar, *J. Eur. Ceram. Soc.* **1998**, *18*, 147.
[26] T. K. Ghose, P. V. Pannir-Selvam, P. Ghosh, *Biotechnol. Bioeng.* **1983**, *25*, 2577.
[27] H.-S. Yang, H.-J. Kim, H.-J. Park, B.-J. Lee, T.-S. Hwang, *Compos. Struct.* **2006**, *72*, 429.
[28] M. Estevez, S. Vargas, H. E. Hagg Lobland, A. de la Isla, W. Brostow, J. R. Rodriguez, *Mater. Res. Innov.* **2006**, *10*, 411.
[29] M. Estevez, S. Vargas, V. M. Castaño, J. R. Rodriguez, H. E. Hagg Lobland, W. Brostow, *Mater. Lett.* **2007**, *61*, 3025.