Curing Behavior and Properties of Rice Husk/Melamine Formaldehyde Composites

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Melamine formaldehyde (MF) composites filled with rice husk powder were prepared by compression molding. The curing processes of the composites with different powder contents and powder particle sizes were studied by dynamic mechanical analysis. Gelation temperature and curing time were subjected to optimization of their mechanical and thermal properties. The rice husk powder loading in the MF matrix and the powder particle size were found to be critical factors governing the curing behavior and properties of the composite. Composites with larger content or smaller powder size had higher gelation temperatures and lower viscosities. The curing times of the composites were also influenced by the powder content. Flexural strength and flexural modulus increased with powder loading in the 20 to 90 mesh particle size range, while notched impact strength decreased. The mechanical properties of the composites decreased to a considerable extent when the fibers were too small to achieve strong interfacial adhesion. Morphological (scanning electron microscopy) and thermal studies (heat deflection temperature) were also conducted.

Keywords: Melamine formaldehyde; Rice husk; Dynamic mechanical analysis

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INTRODUCTION

As the consciousness of environmental protection and resource preservation increases, more and more researchers are turning their attention to renewable bio-materials. Natural, fiber-based lignocellulosic materials are now considered potential substitutes for synthetic fibers for the preparation of reinforced composites (Singha and Thakur 2008). China is one of the largest rice producers in the world, and rice husk (RH) is a major byproduct. Millions of tons of rice husks have had no proper usage, so researchers are working to develop various products from rice husks.

Melamine Formaldehyde (MF) resins have been widely used as adhesives for cellulose-containing materials. Since melamine formaldehyde resins have many advantages, they are used in a wide variety of industrial and consumer products, including packaging and wood-based panels.

Natural fibers are worth considering as possible reinforcing components in composite structures, compared with traditional man-made fibers (Chiellini *et al.* 2004; Hepworth *et al.* 2000; Johansson *et al.* 2012). In particular, composites made from natural fibers and melamine formaldehyde hold promise for product development efforts.

The curing mechanism of melamine formaldehyde is a complex condensation reaction (Hagstrand and Oksman 2001). For a long time, the preparation and characterization of polycondensation resins like UF (urea formaldehyde) and MF (melamine formaldehyde) have been of interest. But there has been little research exploring the curing mechanism of MF/natural fiber composites. Rice husks have components similar to the wood as well as inorganic substances (Ndazi *et al.* 2007a,b; Park *et al.* 2004). These inorganic substances hamper the adhesive strength between the fiber and resin (Kim *et al.* 2006a), and the particle size of the fiber also affects the curing process of the composites. Composites with fibers of different sizes can give rise to different cross-linking densities. All these factors influence the properties of the composites. In this study, the effects of rice husk loading and rice husk particle size on the curing process and properties of MF/RH composites have been investigated. Dynamic mechanical analysis (DMA) was mainly used to study curing behavior of the composites.

EXPERIMENTAL

Materials

The melamine formaldehyde molding powder (MF-PP) used in this study was supplied by Shijiazhuang Yuhua Chemicals (China), which contained 30 wt.% of paper pulp. Rice husks were obtained from Shandong Kangjing Environment Protection and Technology Development, Ltd. (China). The polyethylene wax (PEW) used as an external lubricant was supplied by Wuxi Hongli Plastic Additive Company (China). The ethylene bistearic amid (EBS) used as an internal lubricant and dispersing agent was obtained from Qingdao Sainuo New Materials, Ltd. (China).

Sample Preparation

Rice husks were milled and sieved to obtain three powder particle sizes, namely 20-60 mesh, 60-90 mesh, and 120-200 mesh, before sample preparation. The rice husk powders were dried in an oven at 105 °C for 3 hours. Exact amounts of the MF molding powder, dried rice husks, PEW, and EBS were metered according to the formulation depicted in Table 1. Then, these rice husk powders were blended with the other constituents. The mass of the blended mixture each time was 180 g. Mechanical blending was achieved by a rotational mixing process of the constituents (MF molding powder, rice husk powder, PEW, and EBS) in a container until a uniform mixture was obtained. The speed of the rotating mixer was 29000 r/min, and the mixing time was 5 min.

Table 1. Formulation of Samples

Sample	MF molding powder (MF-PP) (wt.%)	Rice Husk powder (RH) (wt.%)	PEW (phb, parts per hundred of MF-PP/RH blend)	EBS (phb)
MF-PP/RH (50:50)	50	50	3	1
MF-PP/RH (40:60)	40	60	3	1
MF-PP/RH (30:70)	30	70	3	1

Sample Premolding

As the MF resin and rice husk were both supplied in the form of powder, and DMA tests usually need the sample be premolded, a premolding procedure was employed to prepare the DMA test samples (Menard 1999). Generally, thermoset composites are prepared by compression molding. The premolding temperature of the compression molding was carefully checked to reach the melting point of the compound but to avoid pre-curing. The optimal temperature was found to be 80 °C for MF resin (Stark 2010). The premolding time was kept short, and the pressure was 10 MPa. The curing behavior of the premolded MF molding powder sample was measured by DMA (3 °C/min, 1 Hz, three points bending mode). The curing temperature was measured to be 135 °C. As previously mentioned, the addition of rice husk would hamper the adhesive strength between the fiber and resin. In other words, rice husk powder would disturb the curing of MF resin and raise the curing temperature (Kim *et al.* 2006a,b). A high fiber content (over 50 wt.%) would also disturb the premolding procedure of the MF-PP/RH composites. The optimal premolding temperature of the composites was found to be 130 °C. The premolding time was also kept short, about 90 seconds. The molding pressure was 10 MPa.

Dynamic Mechanical Testing

DMA tests were performed on specimens cut from the molded composite materials. The dimensions of the specimens were 40 mm × 4 mm × 4 mm. Testing of samples for DMA was done on a UBM Rheogel Station (Rheogel-E4000). The tests were conducted with the three-point bending mode. Each sample was heated at 3 °C/min from 50 °C to 200 °C at a frequency of 1 Hz and amplitude of 1 μm. Isothermal tests were also conducted to measure the curing times of the composites.

Mechanical Testing

Flexural and Izod impact tests were performed on specimens cut from the composite materials that were cured according to the processing parameters determined by DMA tests. The measurements of flexural strengths were made on a computerized universal testing machine (Shenzhen, New Sansi). The dimensions of the flexural test samples were 80 mm × 10 mm × 4 mm. The flexural tests were conducted in accordance with ASTM D790 at the constant strain rate of 2 mm/min. For impact strengths, the measurements, based on procedure ASTM D256, were executed using a conventional pendulum-type Izod impact tester (Chengde UJ-40). The specimens on the face of the notch (test method A in ASTM D256) were impacted by the striker. At least five specimens were used in each of the mechanical tests.

Morphology Study

The impact fracture surfaces were investigated with a Hitachi S-4800 field emission scanning electron microscope (SEM). The excitation energy used was 10 keV. To achieve good electric conductivity, all samples were coated with gold-palladium by use of a sputter coating instrument.

Heat Deflection Temperature Testing

Heat deflection temperature testing was determined as per ASTM D648. The dimensions of the specimens were 120 mm × 15 mm × 4 mm. The specimens were immersed under load (1.82 MPa) in a heat-transfer medium provided with a means of raising the temperature at 2 ± 0.2 °C/min. The temperature of the medium was measured when the test bar had deflected 0.25 mm. This temperature was recorded as the deflection temperature under flexural load of the test specimen.

RESULTS AND DISCUSSION

Dynamic Mechanical Properties

Dynamic thermal mechanical analysis has been widely used for investigating the structures and dynamic mechanical properties of thermosetting adhesives (Kim *et al.* 2006a,b). During the curing process of a thermoset resin, there are two important events: gelation and vitrification (solidification). DMA is able to detect those two transitions by measuring the change in the mechanical properties. At the macroscopic level, gelation results in an "infinite" viscosity, and therefore it represents a limitation of the processable fluid state (Hagstrand *et al.* 1999).

The point of gelation and time to reach gelation are two important processing parameters. As the tan δ (loss factor) value is closely related to the viscosity changes during the gelation procedure, the tan δ value is generally used to characterize the gelation procedure.

Figure 1 shows the loss factor of composite with different rice husk contents. The loss factor value increased sharply to its maximum value, due to the increase in viscosity, and then decreased as the temperature was further increased. The temperature of the active curing reaction is determined from the maximum tan δ value in many works (Kim *et al.* 2006a,b; Hagstrand *et al.* 1999).

As the fiber content increased in the composites, the peaks of the $T_{\tan \delta}$ value moved to higher temperatures and the maximum tan δ values decreased. The position and height of tan δ peaks are indicative of the structure and properties of composite material (Hameed *et al.* 2007). Therefore, these changes were very possibly related to the viscosity changes during the curing process. Another important factor that could affect the viscosity of the composite system was fiber particle size.

Figure 2 shows the loss factor of composites with different fiber particle sizes. Composites with smaller particles cured at higher temperatures and the maximum tan δ values of the composites were lower. As the temperature was raised, the mobility of the thermoset resin molecules increased. However, the incorporation of rigid fiber particles in the composite system adversely restricted the movement of resin molecules and increased the viscosity.

The results showed that the restriction effect was in inverse proportion to the fiber particle size. The gelation temperature of the composite system shifted to a higher temperature, and the maximum tan δ values became lower as the fiber particle size decreased.

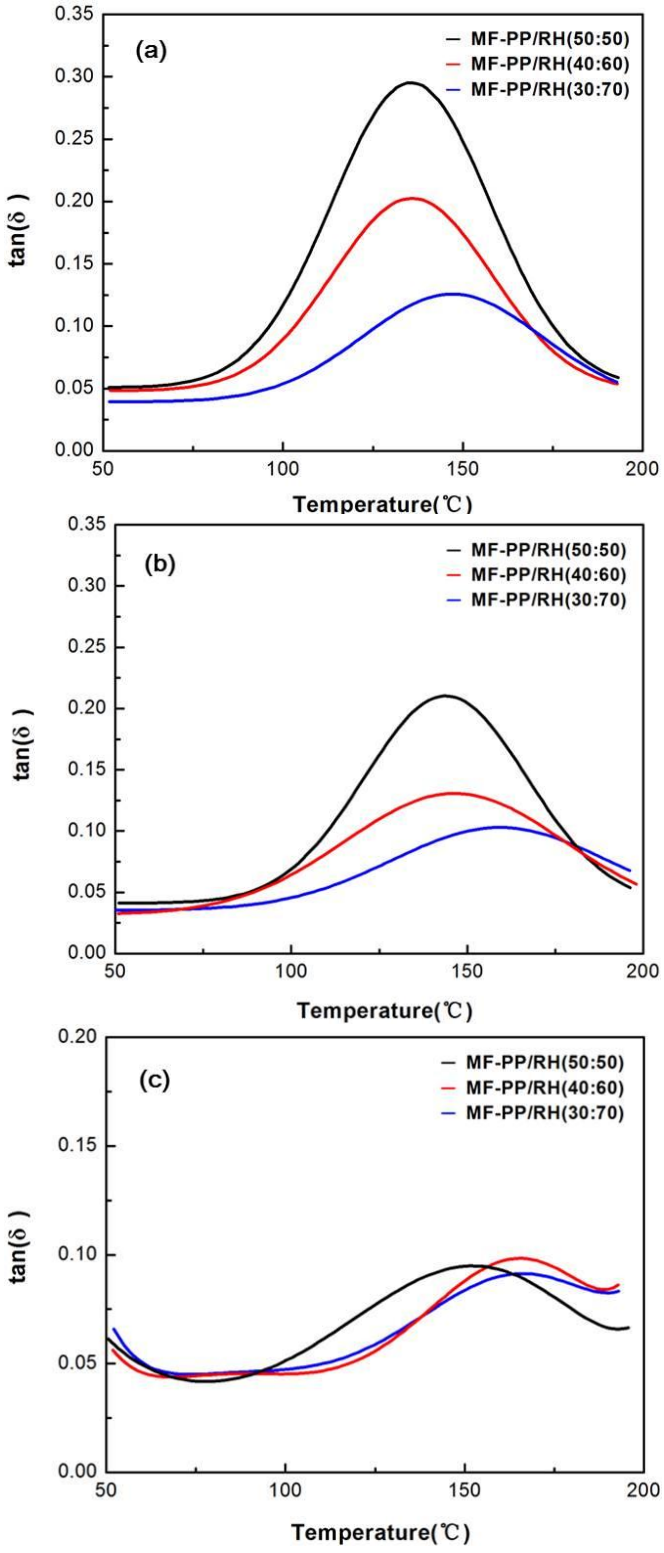

Fig. 1. Loss factor (tan *δ*) of composites with different particle size: (a) 20-60 mesh, (b) 60-90 mesh, (c) 120-200 mesh

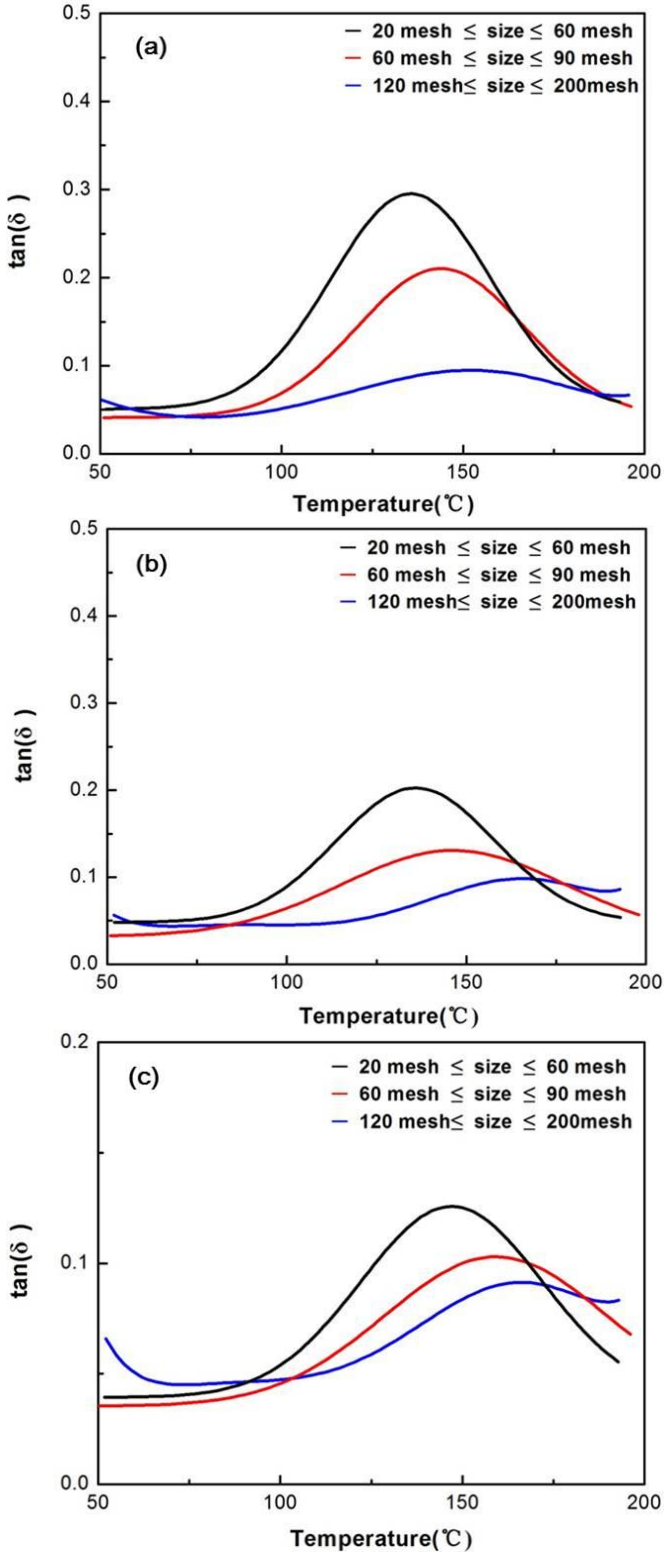

Fig. 2. Loss factor (tan *δ*) of composites with different blend ratios: (a) 50:50, (b) 40:60, (c) 30:70

The results obtained from dynamic mechanical analysis (Figs. 1 and 2) showed that both the content and particle size of rice husk fiber affected the gelation temperature of the composite system. However, the effect of particle size was more significant. The same gelation temperature was selected for composites with the same rice husk fiber size to simplify the processing procedure. The temperatures corresponding to the maximum values of tan δ were 140 °C for MF-PP/RH composites with 20-60 mesh rice husk powder, 150 °C for MF-PP/RH composites with 60-90 mesh rice husk powder, and 165 °C for MF-PP/RH composites with 120-200 mesh rice husk powder. The curing times of composites with different particle sizes and blend ratios were measured by the isothermal DMA method. The isothermal curing temperature was set at the temperature where the gelation point was measured. The results for the curing times are listed in Table 2.

Table 2. Curing Time of Composites with Different Particle Sizes and Blend Ratios

Particle size (mesh)	MF-PP/RH blend ratio	Curing time (minutes)
—	100:0	17-19
20-60	50:50	14-15
20-60	40:60	15-16
20-60	30:70	21-22
60-90	50:50	11-14
60-90	40:60	10-13
60-90	30:70	12-13
120-200	50:50	21-22
120-200	40:60	21-22
120-200	30:70	23-25

The storage modulus (E') changes constantly during isothermal curing of the thermoset resin. The changes in the viscoelastic behavior during isothermal curing result in an inflection of the modulus. When the curing reaction is complete, the storage modulus stabilizes. The time to reach the stabilization of E' is considered the curing time. Because the particle size of rice husk fiber was the same, composites with higher fiber content required a longer time for curing. On the other hand, the curing times of composites with same fiber content and different fiber particle sizes could not be compared, as the curing processing parameters were different.

The properties of the composites are greatly influenced by the curing temperature and curing time. For this reason, optimizing curing conditions is important for thermoset resin research. DMA is not only a useful method to observe changes caused by melting and cross-linking during the curing process, but also a good inspection method to check whether the composite has fully cured. Thermal behavior between the cross-linked material and original material is distinctly different (Stark 2010), so the curing conditions measured above can be checked to see whether or not they are the optimized conditions. Figure 3 shows the DMA results of the composites before and after fully curing.

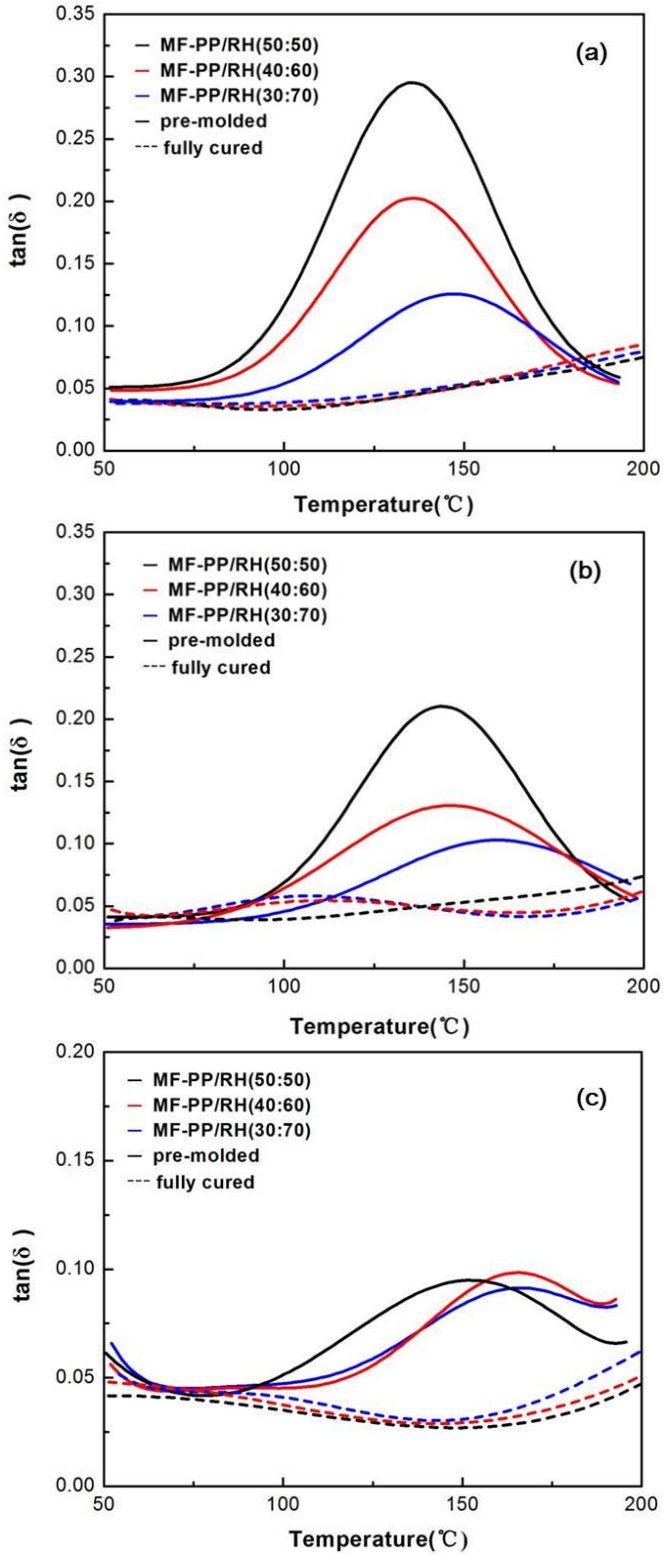

Fig. 3. Loss factor (tan δ) of composite with different particle sizes before and after fully curing: (a) 20-60 mesh, (b) 60-90 mesh, (c) 120-200 mesh

The solid and dashed lines in Fig. 3 represent the pre-molded composites and fully cured composites, respectively. After the curing reaction takes place, the mobility of the thermoset resin molecular is reduced by cross-linking (Stark 2010). The peak of the $T_{\tan \delta}$ value was much lower than the original state. If the curing reaction was complete or near complete, the peak of the $T_{\tan \delta}$ value disappeared. The comparison showed that the curing conditions measured by DMA were optimized conditions (Fig. 3a-c). In case of 60-90 mesh, small peaks of the $T_{\tan \delta}$ value appeared near 100 °C due to the fact that some oligomers remained in the composites.

Mechanical Properties

Melamine formaldehyde resin is a thermoset resin. The high level of cross-linking in thermoset networks leads to inherently brittle materials. However, many methods of modification can be used to improve the toughness and crack resistance of thermoset resins. One successful method is the incorporation of fibers. The fibers play an important role in the impact resistance of the composites, because they interact with the crack formation in the matrix and act as a stress-transferring medium (Mehta *et al.* 2004; Gamstedt *et al.* 2011). Therefore, it is expected that an interaction can be formed between fibers and matrix to improve composite strength and impact behavior (Singha and Thakur 2009; Mehta *et al.* 2004). The results in Table 3 confirm that expectation. Both 20-60 mesh and 60-90 mesh rice husk fibers effectively reinforced the composite systems, as the impact strength improved.

Table 3. Mechanical Properties of MF-PP/RH Composites. Standard Deviations are Shown in Brackets.

Sample* (MF-PP/RH-particle size)	Flexural strength (MPa)	Flexural modulus (MPa)	Notched impact strength (KJ/m^2)
100:0	94.15 (2.54)	10839.70 (68.44)	0.68 (0.09)
50:50-1	48.20 (2.46)	9078.09 (401.89)	1.09 (0.16)
50:50-2	40.37 (1.02)	6630.62 (156.10)	0.99 (0.20)
50:50-3	14.64 (0.77)	2565.25 (38.10)	0.44 (0.01)
40:60-1	50.69 (0.78)	9688.53 (221.31)	0.98 (0.04)
40:60-2	45.87 (4.02)	6951.47 (649.94)	0.93 (0.04)
40:60-3	13.52 (0.92)	2637.98 (152.07)	0.41 (0.02)
30:70-1	52.21 (0.08)	10045.65 (181.21)	0.85 (0.16)
30:70-2	54.20 (3.21)	8554.43 (925.89)	0.69 (0.05)
30:70-3	11.83 (0.20)	2350.93 (120.07)	0.37 (0.02)
* "-1","-2","-3" in this table represent three particle sizes of powders: 20-60, 60-90, 90-120 mesh.			

The results showed that impact strength decreased with rice husk powder loading in both 20-60 mesh and 60-90 mesh cases. This was opposite to the flexural behavior. Flexural strength and modulus increased with rice husk powder loading in both cases. When the fiber particle size was too small, such as 120-200 mesh, the fibers were not

capable of transferring load to one another, which led to worse mechanical properties. It was assumed that more polymer matrix or pressure should be added and applied in order to achieve good fiber reinforcement. In a word, the fiber content and particle size both strongly affected the mechanical properties of the composites. The effect of fiber particle size on the mechanical properties of the composites was more significant.

Morphology

Figure 4 shows the impact fracture surfaces of the composite samples and the reinforcing rice husk fibers. The SEM micrographs show that the interface between fiber and MF matrix was poor and that the fibers were barely covered with matrix resin. Poor adhesion between the fiber and matrix can be a result of the fact that the inorganic substances in rice husk fiber hamper the adhesive strength between the fiber and resin.

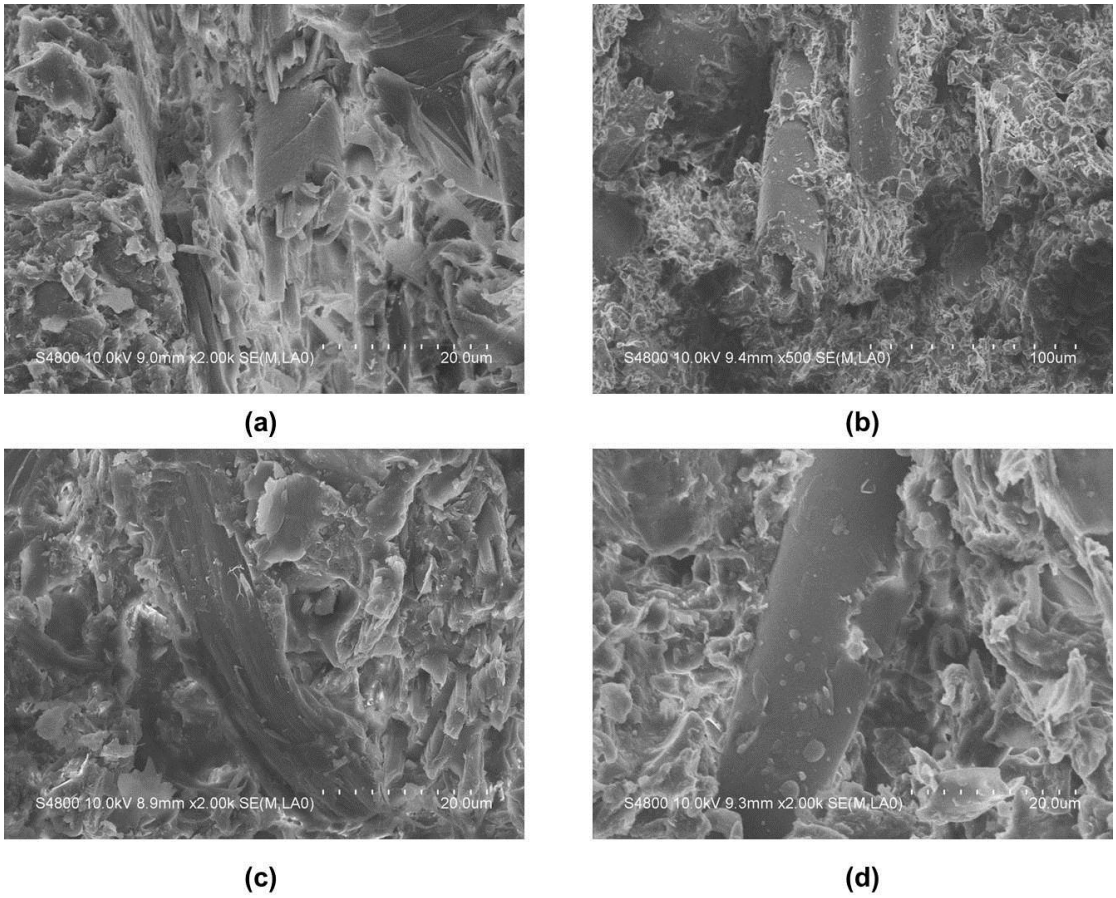

Fig. 4. SEM micrographs of MF-PP/RH composites with different sizes of rice husk powders: (a) and (c) 20-60 mesh, (b) and (d) 120-200 mesh

Comparing Figs. 4(a) and 4(b), better fiber-matrix adhesion was observed when the fiber size was a bit larger. The fiber tended to be broken (Fig. 4(a)) instead of pulling out (Fig. 4(b)) during impaction when the adhesion was strong. Figures 4(c) and 4(d) also confirmed the effect of particle size on the properties of the composites. Figure 4(c) shows that rice husk fiber was embedded in the MF matrix and the matrix held the fiber

tightly. In contrast, the rice husk fiber was loosely bonded to the matrix in Fig. 4(d). The difference between the interfacial adhesion properties of composites with diverse fiber particle sizes explained the distinction between the mechanical properties.

Heat Deflection Temperature

Table 4 shows the heat deflection temperature (HDT) of composites with different particle sizes and blend ratios. The HDT of the MF-PP composite without reinforcing rice husk fibers was measured to be 106.4 °C. It increased with the rice husk powder loading in the MF-PP matrix, except for composites with 120-200 mesh fiber. The particle size of rice husk fiber obviously affected the HDT of the composite system as it did the mechanical properties and morphological structures. As observed from the SEM micrographs, the adhesion between fiber and matrix was poor. Voids were formed around the fibers (Fig. 4(b) and (d)) when the fiber particles were small. The presence of voids decreased the HDT of the composites. More voids could be formed as the rice husk powder loading increased, so the HDT of the composites with 120-200 mesh fiber decreased with increasing fiber loading in the matrix.

Table 4. Heat Deflection Temperature of Composites with Different Particle Sizes and Blend Ratios

Particle size (mesh)	MF-PP/RH blend ratio	HDT (°C)
20-60	50:50	136.9
20-60	40:60	139.4
20-60	30:70	143.2
60-90	50:50	130.7
60-90	40:60	128.1
60-90	30:70	133.6
120-200	50:50	136.7
120-200	40:60	121.5
120-200	30:70	115.7

CONCLUSIONS

1. The content of rice husk powder and powder particle size both affected the curing behavior of MF-PP/RH composites considerably. The gelation temperature increased slightly with rice husk powder loading, while the gelation temperature increased significantly when the particle size decreased. The peaks of the $T_{\tan \delta}$ values were lowered as the viscosities of the composites decreased, due to the increase of rice husk powder content and the decrease of powder particle size.
2. The curing time of the composite system increased with the rice husk powder loading in the matrix.
3. DMA is not only a useful method to observe changes caused by melting and cross-linking during the curing process, but also a good inspection method to check whether the composites are fully cured.

4. The incorporation of 20-60 mesh and 60-90 mesh rice husk powders improved the impact strength of the composites. Flexural strength and flexural modulus of MF-PP/RH composites increased with rice husk powder loading in the matrix, while impact strength decreased. The powder particle size was found to have greater effects on the mechanical properties of MF-PP/RH composites than the content of powder did.
5. The adhesion between rice husk powders and MF matrix was poor. Composites with powders in diverse particle sizes presented different interfacial adhesion properties.
6. The heat deflection temperature of MF-PP/RH composites with 20-60 mesh and 60-90 mesh powders increased with powder loading in the matrix. The HDT of the composites with 120-200 mesh powder decreased with powder loading in the matrix. The HDT of the composites also increased as powder particle size increased.

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REFERENCES CITED

Chiellini, E., Cinelli, P., Chiellini F., and Imam, S. H. (2004). "Environmentally degradable bio-based polymeric blends and composites," *Macromolecular Bioscience* 4(3), 218-231.

Gamstedt, E. K., Sandell, R., Fredrik, B., and Pettersson, T. (2011). "Characterization of interfacial stress transfer ability of particulate cellulose composite materials," *Mechanics of Materials* 43(11), 693-704.

Hepworth, D. G., Bruce, D. M., Vincent, J. F. V., and Jeronimidis, G. (2000). "The manufacture and mechanical testing of thermosetting natural fibre composites," *Journal of Materials Science* 35, 293-298.

Hagstrand, P.-O., Klason, C., Svensson, L., and Lundmark, S. (1999). "Rheokinetical behavior of melamine-formaldehyde resins," *Polymer Engineering and Science* 39(10), 2019-2029.

Hagstrand, P.-O., and Oksman, K. (2001). "Mechanical properties and morphology of flax fiber reinforced melamine-formaldehyde composites," *Polymer Composites* 22(4), 568-578.

Hameed, N., Sreekumar, P. A., Francis, B., Yang, W. M., and Thomas, S. (2007). "Morphology, dynamic mechanical and thermal studies on poly(styrene-co-acrylonitrile) modified epoxy resin/glass fibre composites," *Composites: Part A* 38(12), 2422-2432.

Johansson, C., Bras, J., Mondragon, I., Nechita, P., Plackett, D., Šimon, P., Svetec, D. G., Virtanen, S., Baschetti, M. G., Breen, C., Clegg, F., and Aucejo, S. (2012). "Renewable fibers and bio-based materials for packaging applications - A review of recent developments," *BioResources* 7(2), 2506-2552.

Kim, S., Kim, H.-J., Kim, H.-S., and Lee, H. H. (2006a). "Effect of bio-scavengers on the curing behavior and bonding properties of melamine-formaldehyde resins," *Macromol. Mater. Eng*. 291(9), 1027-1034.

Kim, S., and Kim, H.-J. (2006b). "Thermal stability and viscoelastic properties of MF/PVA hybrid resins on the adhesion for engineered flooring in under heating system; ONDOL," *Thermochimica Acta* 444(2), 134-140.

Mehta, G., Mohanty, A. K., Misra, M., and Drzal, L. T. (2004). "Effect of novel sizing on the mechanical and morphological characteristics of natural fiber reinforced unsaturated polyester resin based bio-composites," *Journal of Materials Science* 39(8), 2961-2964.

Menard, K. P. (1999). *Dynamic Mechanical Analysis – A Practical Introduction*, CRC Press, Boca Raton, Florida, USA.

Ndazi, B. S., Nyahumwa, C., and Tesha, J. (2007a). "Chemical and thermal stability of rice husks against alkali treatment," *BioResources* 3(4), 1267-1277.

Ndazi, B. S., Karlsson, S., Tesha, J. V., and Nyahumwa C. W. (2007b). "Chemical and physical modifications of rice husks for use as composite panels," *Composites: Part A* 38(3), 925-935.

Park, B.-D., Wi, S. G., Lee, K. H., Singh, A. P., Yoon, T.-H., and Kim, Y. S. (2004). "X-ray photoelectron spectroscopy of rice husk surface modified with maleated polypropylene and silane," *Biomass and Bioenergy* 27(4), 353-363.

Singha, A. S., and Thakur, V. K. (2008). "Fabrication and study of lignocellulosic *Hibiscus sabdariffa* fiber reinforced polymer composites," *BioResources* 3(4), 1173-1186.

Singha, A. S., and Thakur, V. K. (2009). "Study of mechanical properties of urea-formaldehyde thermosets reinforced by pine needle powder," *BioResources* 4(1), 292-308.

Stark, W. (2010). "Investigation of curing behavior of melamine/phenolic (MP) thermosets," *Polymer Testing* 29(6), 723-728.

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