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# Synergistic effect of coupling agents and fiber treatments on mechanical properties and moisture absorption of polypropylene–rice husk composites and their foam

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ABSTRACT

Rice husks and polypropylene were applied as the fibers and matrix, respectively, to make composites. Polypropylene-grafted maleic anhydride (PP-g-MA) and styrene ethylene butadiene styrene-grafted maleic anhydride (SEBS-g-MA) were used as coupling agents. The rice husks were also treated with NaOH, silane, or NaOH + HCl + silane to enhance the effect of the coupling agents. Using a combination of 2 wt% PP-g-MA and 1 wt% SEBS-g-MA, the impact strength of the composite increased, but the tensile strength and modulus were not reduced relative to the use of PP-g-MA alone. The three treatments – NaOH, silane and NaOH + HCl + silane – and added coupling agents improved the impact strength and decreased the moisture absorption rate of the composites except for those subjected to the alkaline treatments. The foaming results showed that adding coupling agents improved the cell structure and reduced the density of the foam.



## 1. Introduction

NF have many advantages, e.g., low density, low cost, and highly specific mechanical properties. The modulus of natural fibers can be as high as 6–80 GPa, comparable to those of glass fibers [1]. However, NF density is significantly lower than that of glass fibers. The high modulus of NFs comes from the high cellulose content. Cellulose possesses a Young's modulus of $\sim$140–250 GPa, and it usually occupies more than 60 wt% of the NFs [2]. Due to their renewable and biodegradable characteristics, NFs are used to reinforce composites and this can reduce the impact on the environment. The low energy consumption and low carbon footprint of making natural fibers is considered sustainable.

There are many kinds of NFs, such as bamboo, sisal, jute, hemp, flax, and rice husks, and their use usually depends on their cost and availability. In this study, rice husks are used as fillers because they are abundant and usually considered as agricultural waste in eastern Asia. Rice is grown as an annual plant, and it can grow to 1–1.8 m tall, depending on the variety and soil fertility. Rice husks usually contain 35–45 wt% cellulose, 19–25 wt% hemicellulose, 20 wt% lignin, 14–17 wt% wax, and 15–17 wt% silica [3]. Like other NFs, rice husks easily absorb moisture because they contain cellulose. It is noteworthy that silica is not seen in most natural fibers. The high silica content in rice husks provides high stiffness and improves the flame retardant characteristics of polymer/rice husk composites [4,5]. Therefore, the use of rice husks as a filler of composites has gradually increased because this solves the problem of agricultural waste use and produces value-added composites. This research is especially important in Asia, where most of the world's rice is produced.

Rice is a major grain crop and is the staple food for more than half of the human population. According to a survey by the Food and Agriculture Organization of the United Nations (FAO) in 2012, the annual rice production reached 724.5 million tons, of which $\sim$655.1 million tons were produced in Asia [6]. Therefore, as an agricultural waste, rice husks could cause environmental problems. The current applications of rice husks are as feedstock, fertilizer, biodiesel, incineration, and pillow stuffing. The idea of using rice husks or other agricultural waste as fillers in composites perhaps proposed by researchers as early as in 1985 [7]. However, this research was not dynamic until 2000. Before 2000, Fuad et al. were almost the only research group using rice husk ash but not rice husks as the filler of composites [8,9]. Although the calorie value of rice husks is low, it is common practice to burn rice husks and use them as fuel for industrial purposes. The byproduct, rice

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husk ash, contains nearly 95 wt% silica [10]. Since the mechanical properties of silica are significantly higher than those of polymers, one of the potential applications for rice husk ash is to use it as a filler to improve the mechanical properties of polymer composites. These days, the biodegradability of polymer composites is becoming more and more important, and researchers are starting to use rice husks for composite applications. Yang et al. did a series of studies comparing the mechanical and thermal properties of composites made of wood flour and rice husks. The results showed that although the mechanical properties of rice husks are slightly lower than those of wood flours [11], rice husks provide better thermal stability than wood flours owing to the presence of silica [12].

Polypropylene (PP) is a thermoplastic polymer with a density of 0.81–0.91 g/cm$^3$, which is lower than that of other plastics such as acrylonitrile butadiene styrene (ABS), polyethylene (PE), polystyrene (PS), polyvinyl chloride (PVC), etc. PP also has higher tensile strength and modulus and better thermal stability than other plastics. The melting point of industrial-grade PP is 160–166 °C [13]. Thus, the service temperature of PP can be as high as 100–120 °C. The applications of PP include automotive, appliances, daily necessities, furniture, packaging, etc. Additionally, PP possesses excellent chemical resistance. In most cases, PP is non-reactive and it cannot be dissolved by the majority of solvents.

Owing to the biodegradable nature of biofibers, automobile manufacturers such as Audi, Ford, and BMW in Europe have introduced natural fibers such as bast fibers and wood flours to replace glass fibers in cars [14]. Although polypropylene–rice husk composites have been used for applications such as utensils, furniture, and building and construction materials, the use of rice husks for automobile applications has not been reported. With proper design, natural fiber composites (NFCs) could become a fashion product. For example, recycled PP can be compounded with 35 wt% rice husks and injection molded to form a cellular phone case, wine bottle packaging, or sun glasses [15]. The concept of integrating fashion design with green/renewable products may open up a new route for recycled plastics and natural fibers.

A major problem in making polymer/NF composites is the incompatibility between the fiber and the polymer matrix. Since polymers are hydrophobic and natural fibers are hydrophilic, the compatibility between PP and natural fiber is poor. Compounding two incompatible substances may cause fibers to agglomerate, and there is a poor bonding between the polymer matrix and the fibers that may result in poor mechanical properties and a high rate of moisture absorption, which could be detrimental to the composites. Also, biofibers tend to suffer fungal attack under humid conditions, and absorbing moisture may swell the fibers and lead to swelling of the composites.

The problem can be solved by using coupling agents. Coupling agents are block copolymers that react with the hydroxyl groups on the fiber surface to enhance the compatibility between the fiber and the polymer. There are two ways to modify the surface properties of natural fibers. First, coupling agents containing isocyanates, silane, polymers grafted with maleic acid, and triazine can be used as polymer additives during compounding. Secondly, before compounding, the surface of the fibers can be modified with chemicals used to enhance compatibility. As compared to using polymer additives, surface modification would be more efficient than using a coupling agent. However, it is less cost effective and more time consuming. Surface modification is different from adding coupling agents. Surface modification is a way of altering the hydrophilicity of the fiber surface. Fiber treatments include physical methods and chemical methods [16]. Corona or plasma treatments are considered physical treatments. Chemical methods include silane treatment, alkaline treatment, acetylation, maleated coupling, and enzyme treatment [17]. In the treatments mentioned above, some of them add functional groups onto the surface of the fibers, whereas others remove the weak parts of the natural fibers. For example, alkaline treatment removes the weak parts of the natural fibers, i.e., hemicellulose and lignin, and thus improving the mechanical properties of the fibers [18], whereas silane treatments improve the functionality of the fibers and make them compatible with polymers. In addition to coupling agents or surface modification, the type of compounding equipment or changes to the processing variables may also reduce the rate of water absorption [19,20]. The kinetics of moisture absorption are determined by two factors. One is the diffusion coefficient and the other is the equilibrium moisture content. The diffusion coefficient determines the time needed to reach the equilibrium moisture. The equilibrium moisture may affect the final dimensions and mechanical properties of the composite.

The density of most biofibers, including rice husks, is ~1.2–1.5 g/cm$^3$, which is significantly higher than that of solid wood [1]. To mimic the density of wood and other natural fibers, it is reasonable to foam NFCs during processing. It is especially desirable to foam NFCs for automobile applications since it could significantly improve the fuel efficiency of cars [14]. The foaming of natural fiber composites can be achieved by various processing techniques such as batch, injection molding, extrusion, and compression molding [21]. In these processes, both physical and chemical blowing agents are applied. Carbon dioxide is considered a possible candidate as a physical blowing agent because it possesses relatively higher solubility than other inert gas in most polymers and because it contributes far less to the greenhouse effect as compared to traditional blowing agents such as chlorofluorocarbons. In this study, carbon dioxide was used as the blowing agent in order to foam PP–rice husk composites using the batch foaming method.

## 2. Experimental

### 2.1. Materials

Rice husk flours of ~35–40 mesh were provided by Miniwiz Sustainable Energy Development Co. Ltd., Taiwan. Polypropylene, PP, (PP TAIRIPRO K1023) was purchased from Formosa Chemicals & Fibre Corporation, Taiwan. The melt flow index of PP is 25 g/10 min at 230 °C and 2.16 kg. The coupling agent PP-g-MA (trade name Polybond® 3200) was purchased from Chemtura, USA. The maleic anhydride content of PP-g-MA is 1 wt%. The SEBS-g-MA (trade name FG-1901) coupling agent was purchased from Kraton, USA. The maleic anhydride content of FG-1901 is 1.7 wt%. Before the materials were compounded, rice husks, PP, and the coupling agents were dried in a vacuum oven at 80 °C for 12 h. It is worth noting that the coupling agent content is based on the weight percentage of rice husk rather than the total weight of the composite.

The rice husks, PP, and additives were compounded using a Brabender plasticorder (PLE-331) internal mixer with a speed of 50 rpm at 180 °C for 5 min. After mixing, the materials were quenched in a water bath. The compounded materials were then ground into powder using a pulverizer (RT-02A, Rong Tsong Precision Technology). The ground powders were dried at 85 °Cfor 12 h and then injection molded using a Thermo Haake Minijet injection molding machine with an injection temperature of 180 °C and a pressure of 750 bar (75 MPa) to produce ASTM D638 Type IV samples and ASTM D256 samples for mechanical testing.

a. Mechanical properties testing

The tensile and impact strength and stiffness properties of these samples were measured using a Tinius Olsen H5KS universal testing machine and a CEAST digital impact tester. The tensile strength was analyzed according to ASTM D638, whereas the impact test was carried out according to ASTM D256. The strain rate of the