Preparation and flexural properties of biomimetic laminated boards made from starch and maize stalk fiber

Zhang Fu[1], Wu Na[2], Tong Jin[3], Zhou Jiang[3], Yang Xin[4], Ma Yunhai[3], Chen Donghui[3], Sun Jiyu[3]

(1. *College of Vehicle and Motive Power Engineering*, *Henan University of Science and Technology*, *Luoyang* 471003, *China*;
2. *Department of Automotive Engineering*, *Shandong Jiaotong University*, *Jinan* 250023, *China*;
3. *Key Laboratory of Terrain-Machine Bionics Engineering* (*Ministry of Education, China*) *and College of Biological and Agricultural Engineering*, *Jilin University at Nanling Campus*, *Changchun* 130025, *China*;
4. *College of Mechanical and Electrical Engineering*, *Hebei Agricultural University*, *Baoding* 071001, *China*)

Abstract: In this study, maize stalk tegument separated from the maize pith was crushed to obtain the fiber. The cross-linking maize starch adhesives considering four main factors (water content, gelatinization temperature, NaOH as gelatinization agent and $Na_2B_4O_7·10H_2O$ as cross-linking agent) with three levels were prepared based on an orthogonal test scheme $L_9(3^4)$ in order to increase the water-resisting property and the bonding strength of the common maize starch adhesives. The bonding properties of maize starch adhesives were characterized using shearing strength under compression loading. Physical models of fiber reinforced composites were established according to the microstructure analysis of the four species of insects' elytra including *Protaetia orentalis*, *Copris ochus* Motschulsky, *Anoplophora chinensis* and *Cytister bengalensis* Aube, which will provide the biomimetic models for the biomimetic laminated boards. The maize stalk fiber biomimetic laminated boards were prepared based on the structural models of the elytra material. The flexural strength and flexural elastic modulus of the biomimetic boards were examined. The results showed that the flexural strengths of the single layer jute fiber, -reinforced maize stalk fiber boards and the dual layer jute fiber reinforced maize stalk fiber boards are higher than those of the common maize stalk fiber boards and the other three groups of jute fiber hybrid reinforced stalk fiber boards because of the biomimetic laminated design.

Keywords: maize stalk, biomimetic, elytra, starch, laminated board, flexural property
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1 Introduction

With increasing applications of plastics, the environmental pollution from plastic wastes has become a serious problem. Biodegradable materials have been developed for several decades aiming at reducing pollution of plastic wastes. The plant fiber as natural polymers are abundant and have many special properties, such as high aspect ratio, high specific strength, high specific surface area, low density and bio-degradation. Stalk fiber is one of the important plant fibers. Compared with other fiber reinforced composite materials,

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Authors: Zhang Fu(1978－), PhD, master student supervisor, College of Vehicle & Motive Power Engineering, Henan University of Science and Technology, Luoyang 471003, China. Tel: +86-379-64231480-87, Fax: +86-379-64231739. Email: zhangfu30@126.com. **Wu Na,** Ph.D, associate prof., Email: wuna1978@163.com. **Zhou Jiang,** Ph.D, prof., Email: jiang.zhou@jlu.edu.cn. **Yang Xin,** Ph.D, associate prof., Email: yangxin@mail.hebau.edu.cn. **Ma Yunhai,** Ph.D, associate prof., Email: myh@jlu.edu.cn. **Chen Donghui,** Ph.D, prof., Email: dhchen@jlu.edu.cn. **Sun Jiyu,** Ph.D, associate prof., Email: sjy@jlu.edu.cn

Corresponding author: Tong Jin(1957－), PhD, Prof, dean, Key Laboratory of Terrain-Machine Bionics Engineering (Ministry of Education, China) and College of Biological and Agricultural Engineering, Jilin University at Nanling Campus, Changchun 130025, China. Tel.: +86-431-85095730; Fax: +86-431-85095730. Email: jtong@jlu.edu.cn

the stalk fiber reinforced composite materials have unique advantages, such as lighter weight, lower price, better machinability and biodegradation[1-4].

Several types of adhesive resins have been used to make stalk particleboard. The more commonly used resins are UF (Urea-formaldehyde Resin), MF (Melamine-formaldehyde Resin) and PF (Phenol-formaldehyde Resin). However, in addition to the possible environmental problem resulting from the toxic formaldehyde emissions of particleboard, these resins have poor bondability with stalks. The reason is that the inherent nonpolar and hydrophobic characteristics of stalk surface due to silica and wax component were not compatible with the polar and hydrophilic nature of the UF, MF and PF resins. Starch adhesives have been used to replace UF, MF or PF to reduce the emission and bonding problems of the particleboard[5,6].

In order to obtain a suitable method for the structural design of boards, a new design technique is needed. Many examples of composite materials existing in nature possess the optimal structures for their environments through their natural evolution. For this reason, the structures of the beetle elytra were applied in order to simulate and develop biomimetic composite materials in the current research[7]. It is believed that the bionics is a technological science to study the structures, characteristics, elements, behavior, and interaction of the biologic system, in order to provide the new design idea, working principle, and system structure for the engineering[8,9]. Within the elytra of insects, researchers have found laminated structures in which the forewing proteins act as the soft matrix, while the chitin fiber act as the reinforcing fiber. Both the laminated arrangement of the chitin fiber and the mechanical characteristics of these equiangular laminating layers of the biomimetics composites have been reported previously[10,11].

The main objectives of this research were to study the preparation method of the biomimetic laminated boards made from starch and maize stalk fiber, and characterize the flexural properties of maize stalk/maize starch biomimetic laminated boards as affected by starch modification/denaturation, the increase of the reinforced jute fiber and the biomimetic design methods.

2 Experimental materials and methods

2.1 Experimental materials and equipment

The maize starch was obtained from the Qishen Food Company of Jilin Province, China. The NaOH, $Na_2B_4O_7 \cdot 10H_2O$ (provided by Beijing Chemical Plant) and C_2H_5OH (provided by Beijing Chemical Plant) were analytical reagents. The starch-water suspension was uniformly mixed and gelatinized by model JB-3 timing and constant-temperature control magnetic whisk.

The macroscopical characteristics and the microstructure characteristics of the experimental insects were investigated by OLYMPUS SZX12 stereo microscope and JSM-5310 SEM respectively. Corn stalk tegument separated from the corn pith was crushed to obtain the fiber by JWF-250 universal disintegrator (made in China) and SZS three-dimensional vibrator (made in China). The biomimetic boards were prepared by JF805R mixer (Equipment Engineering Research Institute, Jilin University, China) and JFY50 hot-press machine (Equipment Engineering Research Institute, Jilin University, China), and the flexural properties of biomimetic laminated boards were measured with WDW-20 computer-control electron universal tester (Shanghai Hualong Test Instruments Co., LTD).

2.2 Biological prototype

The experimental object was male *Protaetia orentalis* as shown in Figure 1, which was caught from the suburb of Changchun City, Jilin Province, China. The width of body was 18−24 mm and the length was 8−14 mm. The macroscopical characteristics of *Protaetia orentalis* were observed by using OLYMPUS SZX12 stereo microscope. The linear and puncture particles can be clearly seen from the elytra surface.

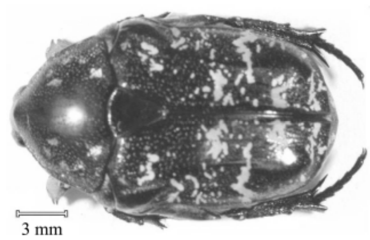


Figure 1 Photograph of *Protaetia orentalis*

The microstructure characteristics of the elytra sample were investigated by using SEM[12]. The elytra were peeled from the body of *Protaetia orentalis*, which was dried at 80℃ by an oven. The elytra samples were fixed on a circular metal sheet with glue, and then were coated by ion sputtering equipment. A JSM-5310 SEM was used to observe the section microstructures of the elytra.

2.3 Preparation of maize stalk fiber

Maize stalk tegument separated from the maize pith was crushed to obtain the fiber. The figures of the maize stalk tegument separated from the maize pith are shown as Figure 2. Corn stalk tegument separated from the corn pith was crushed to obtain the fiber by JWF-250 home universal disintegrator and SZS three-dimensional vibrator.

a. Inside b. Outside

Figure 2 Maize stalk tegument separated from the maize pith figures.

2.4 Preparation of maize starch adhesives

The cross-linking maize starch adhesives considering four main factors (water content, gelatinization temperature, NaOH as gelatinization agent and $Na_2B_4O_7{\cdot}10H_2O$ as cross-linking agent) with three levels were prepared based on an orthogonal test scheme $L_9(3^4)$ in order to increase the water resisting property and the bonding strength of the common maize starch adhesives. The levels and factors of the experiments were researched, and range analysis of testing results and variance analysis of experimental results were conducted[13]. The bonding properties of maize starch adhesives were characterized using shearing strength under compression loading (GB/T17517-1998, adhesives-wood to wood adhesive bonds-determination of shear strength by compression loading). The best combination of factors based on starch of 10 g, i.e. 125 g of water content, 80℃ of gelatinization temperature, 0.10 g of gelatinization agent and 0.03 g of cross-linking agent, were tested and verified, and the shearing strength by compression loading was 1.425 MPa[13]. It was found from variance analysis that the effect extent of each factor on shearing strength by compression loading was determined. The results show that the water content and gelatinization temperature had an evident effect on the bonding properties of maize starch adhesives, but the gelatinization agent and cross-linking agent had no significant influence. The maize starch adhesives (The best combination of factors based on starch of 10 g, i.e. 125 g of water content, 80℃ of gelatinization temperature, 0.10 g of gelatinization agent and 0.03 g of cross-linking agent) provided adhesive for the preparation of the biomimetic boards[13].

2.5 Preparation of the biomimetic laminated boards

2.5.1 Modification of jute fiber

The jute fiber must be modified in order to maintain compatibility with the adhesive and alkaline and oxidizing agents which are the commonly used reagents[14]. In this study, chemical treatments were applied to remove the wax and ash from the stalk surface. The long jute fiber was reduced to a length of 1−2 cm with shears. A solution with 17% NaOH was prepared And the jute fiber was added at a ratio of 1:10, and the solution was stirred for 2 h at room temperature, and the treated jute fiber was then washed five times using distilled water and dried to constant weight in an oven at 120℃. The unmodified shape figure of the jute fiber is shown in Figure 3 And the modified shape figure of the short jute fiber is shown in Figure 4. The diameter of the modified short jute fiber was measured by microscope, and the test results showed that the average diameter of the modified short jute fiber was 400 μm, and the diameter ranged from 300 μm to 850 μm.

Figure 3 Unmodified shape figure of the jute fiber

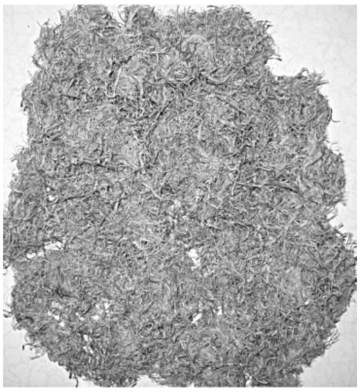


Figure 4 Modified shape figure of the short jute fiber

2.5.2 Preparation of boards and three biomimetic structures

The best combination of factors of maize starch adhesives based on starch of 10 g, i.e. 125 g of water content, 80℃ of gelatinization temperature, 0.10 g of gelatinization agent (NaOH) and 0.03 g of cross-linking agent ($Na_2B_4O_7 \cdot 10H_2O$) was used as adhesive for the preparation of the biomimetic boards. One hundred-gram stalk fiber was mixed with the adhesive solution at a ratio of 1:1 for 10 min by JF805R remiform mixer, and then the mixture was dried for five minutes at room temperature, then pressed into particleboard using a 150×150 mm^2 steel mold and JFY50 hot-press machine. The biomimetic boards were pressed at 7 MPa and 150℃ based on the preparation parameter figures of biomimetic laminated boards shown in Figure 5. Blowhole may occur due to the large amount of moisture vapor accumulated in the biomimetic boards.

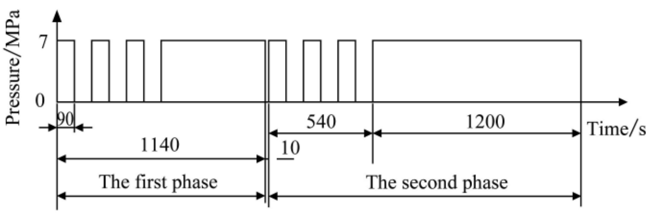


Figure 5 Preparation parameters of biomimetic laminated boards

The maize stalk fiber biomimetic laminated boards were prepared learning from the structural models of the elytra material[15]. As is well known, the exact same density of the boards is difficult to prepare with different preparation parameters. In this research, the density of the boards ranged from 1.19 g/cm^3 to 1.27 g/cm^3. The density of biomimetic boards is shown in Table 5[13]. Biomimetic laminated boards are of three types including the single layer jute fiber reinforced maize stalk fiber boards (Figure 6), the dual layer jute fiber reinforced maize stalk fiber boards (Figure 7), and three groups of jute fiber hybrid reinforced maize stalk fiber boards (Figure 8). After the preparation of the single layer jute fiber reinforced maize stalk fiber boards was concluded, the raw materials of maize stalk fiber boards were divided into two equal parts. One part of the raw materials of maize stalk fiber boards was loaded in the female die (under layer) uniformly, then, 2.5 g of modified jute fiber was loaded on the mold (middle layer), finally, the other part of the raw materials of stalk fiber boards was loaded on the mold (upper layer) uniformly. The preparation of the dual layer jute fiber reinforced maize stalk fiber boards included: firstly, the raw materials of maize stalk fiber boards were divided into three equal parts, the first part of the raw materials of maize stalk fiber boards was loaded on the female die (first layer)uniformly, then, 2.5 g of modified jute fiber were loaded on the mold (second layer), secondly, the second part of the raw materials of maize stalk fiber boards was loaded on the mold (third layer) uniformly, another 2.5 g of modified jute fiber was loaded on the mold (fourth layer), and lastly, the third part of the raw materials of maize stalk fiber boards was loaded on

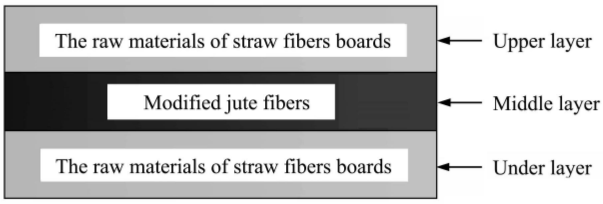


Figure 6 Single layer jute fiber reinforced maize stalk fiber boards

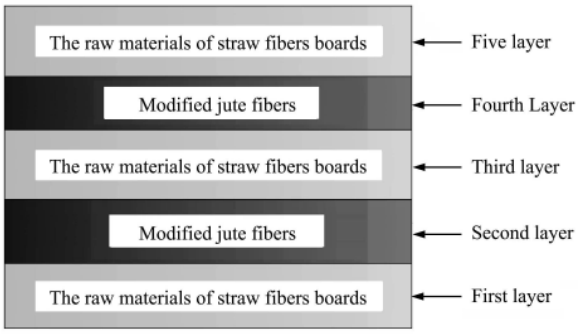


Figure 7 Dual layer jute fiber reinforced maize stalk fiber boards

the mold (five layer)uniformly. The preparation step of three groups of jute fiber hybrid reinforced maize stalk fiber boards was that the raw materials of maize stalk fiber boards were mixed uniformly with 3 g, 5 g and 7 g modified jute fiber respectively.

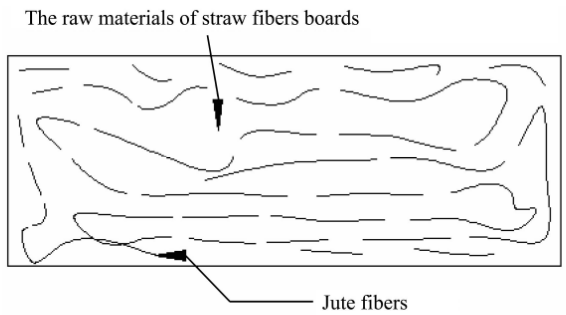
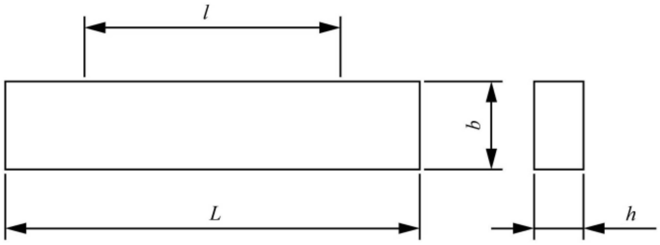


Figure 8 Jute fiber hybrid reinforced maize stalk fiber boards

2.6 Principle for testing the biomimetic maize stalk fiber boards

Biomimetic maize stalk fiber boards were cut into rectangular strips for three-point flex measurement. Samples were conditioned at 60% relative humidity (RH) at 20℃ for 240 h before testing. Mechanical properties were determined by following GB standard method (GB3356-1999, Test methods for flexural properties of unidirectional fiber reinforced plastics) with WDW-20 computer-control electron universal tester. The radius of the pressure head was 5 mm (*R*), and the radius of the abutment was 2 mm (*r*). The ratio of the span to the thickness was 16. The pressure head speeds were 2 mm/min for three-point flex. Reported values are the average of five specimens. The dimension of the samples of the biomimetic laminated boards and the test method for the flexural property of the biomimetic laminated boards are shown in Figure 9 and Figure 10.



L—the sample length, mm; *l*-the sample span, mm; *h*—the sample thickness, mm; *b*—the sample width, mm

Figure 9 Sample dimension of the biomimetic laminated boards

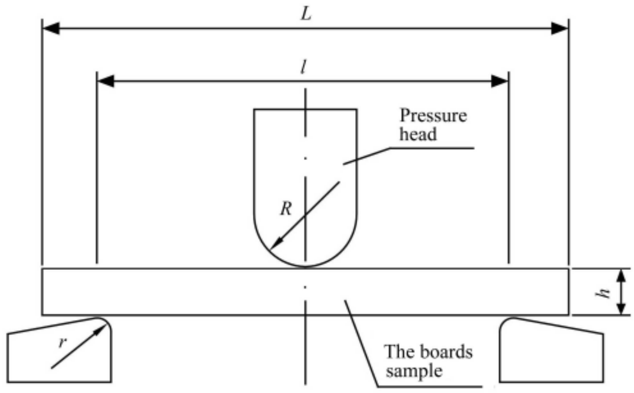


Figure 10 Test method of the flexural property of the biomimetic laminated boards

3 Results and discussion

3.1 Biomimetic models

The orthogonal laminated structure in the elytra of *Protaetia orentalis* was studied[12]. The fiber of each layer was arranged in parallel showing the anisotropy between the fiber of each layer. The fasciculus of helicoidal structure was found inside the elytra. The elytra of *Protaetia orentalis* is the laminated composite materials, which is mainly composed of chitin fiber and protein. Many layers at certain arrangement direction formed with the chitin fiber and protein matrix, and the helicoidal laminated structure were found from the microstructure of the elytra. The elytra can possess the high toughness and strength owing to the existence of the laminated structure. The laminated composite materials were linked with the interface of the layer. The interface can transfer loadings to the adjacent layers when an external force is applied on the laminated composite, it can also generate the connection between the layers to ensure that the elytra has enough strength and toughness. The existence of helicoidal laminated structure can ensure that the elytra has preferable flexural strength and the elytra will not be easily broken in flight[12].

In addition, the microstructures of the elytra materials of three other species of insects, *Copris ochus* Motschulsky, *Anoplophora chinensis* and *Cytister bengalensis* Aube, were examined by SEM. The results showed that the elytra were composed of laminated composite materials and the structures of their fibers or fiber bundles have varied types, including T type structure, the branch fiber structure, the orthogonal laminated structure, the helicoidal structure, the hole structure and the reticular structure. The structural feature of the insect elytra material would provide some biomimetic models for the structural design of the biomimetic composite materials with light weight and high strength[15].

There are many types of fiber reinforced composite boards based on the different structures of biological composite materials, such as continuous fiber and the short fiber reinforced composites, unidirectional continuous fiber reinforced composites[0], two-directional continuous fiber reinforced composites [0/90], two-dimensional continuous fiber reinforced composites [0/90/0], two-directional continuous fiber reinforced composites [0/90/90/0], multidirectional continuous fiber reinforced composite [0/45/90/-45/0], multidirectional continuous fiber reinforced composite [0/45/90], unidirectional chopped fiber reinforced composites, flat random distribution short fiber reinforced composites and space random distribution short fiber reinforced composites[16]. The physical models of monolayer random distribution short fiber reinforced composites, bi-layer random distribution short fiber reinforced composites and space random distribution short fiber reinforced composites are shown in Figure 11, Figure 12 and Figure 13, respectively[15]. The physical models will provide original models for the structural design of biomimetic stalk fiber boards including laminated composites and fiber reinforced composites.

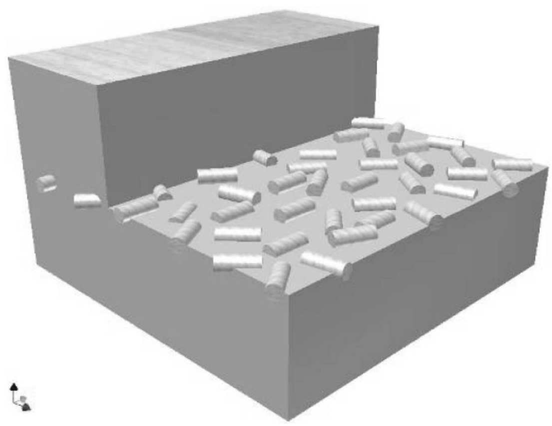


Figure 11 Physical models of monolayer random distribution short fiber reinforced composites

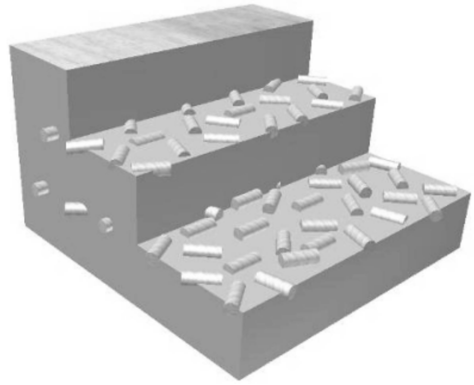


Figure 12 Bi-layer random distribution short fiber reinforced composites

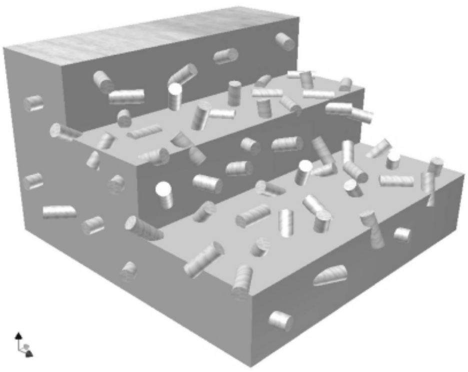


Figure 13 Physical models of space random distribution short fiber reinforced composites

3.2 Distribution of the fiber dimensions

The figures of the maize stalk fiber and the size figures of maize stalk fiber are shown in Figure 14 and Figure 15 respectively. The distributions of the fiber dimensions were measured and it was found that the fiber used for tests have 28.35%wt of 2.0–5.0 mm in diameter, 9.29%wt of 1.0–2.0 mm in diameter, 34.99%wt of 0.5–1.0 mm in diameter and 27.36%wt of less than 0.5 mm in diameter. The moisture content of the maize stalk fiber was 8.05%wt.

Figure 14 Maize stalk fiber

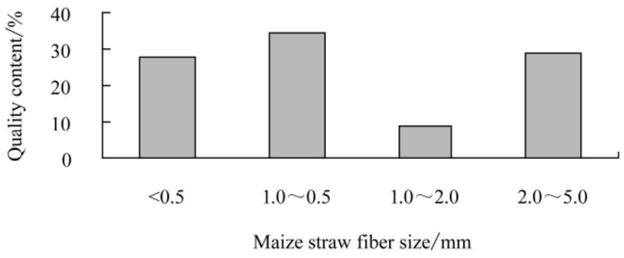


Figure 15 Size figures of maize stalk fiber

3.3 Flexural properties of the biomimetic boards

The maize stalk fiber biomimetic laminated boards were prepared based on the structural models of the elytra material. The flexural strength and flexural elastic modulus of the biomimetic composites were examined. The flexural strength and the flexural elastic modulus of the biomimetic boards are shown in Table 1. As can be seen in Table 1, the results showed that the flexural strengths of the single layer jute fiber reinforced maize stalk fiber boards and the dual layer jute fiber reinforced maize stalk fiber boards are higher than those of the common maize stalk fiber boards and three groups of the jute fiber hybrid reinforced maize stalk fiber boards, and the flexural strength of the dual layer jute fiber reinforced maize stalk fiber boards is higher than that of the single layer jute fiber reinforced maize stalk fiber boards. Improvement on the flexural strength of the biomimetic boards was ascribed to the biomimetic design, the jute fiber as the biomimetic layer added to the maize stalk fiber boards had improved the strength of the maize stalk fiber, so the flexural strengths of the biomimetic boards were improved obviously. Whereas, the flexural strength of the jute fiber hybrid reinforced maize stalk fiber boards improved apparently relative to the cross-linking starch/maize stalk fiber boards. On the contrary, the flexural strengths of the second group of jute fiber hybrid reinforced maize stalk fiber boards (5 g jute fiber) and the third group of jute fiber hybrid reinforced maize stalk fiber boards (7 g jute fiber) were lower than that of the cross-linking starch/ maize stalk fiber boards, which indicated that the laminated biomimetic structures were better than the hybrid biomimetic structures of the experimental results. The flexural elastic modulus of the dual layer jute fiber reinforced maize stalk fiber boards was higher than that of the cross-linking starch/maize stalk fiber boards. The flexural elastic modulus of other biomimetic boards was not improved compared with the cross-linking starch/maize stalk fiber boards, and the possible reason was that the optimization of the flexural strength was a more important consideration than the optimization of the flexural elastic modulus in optimizing the flexural properties of the cross-linking starch/ maize stalk fiber boards.

Table 1 Flexural properties of the biomimetic boards

Types of biomimetic boards	Flexural strength/MPa	Flexural elastic modulus/MPa
The cross-linking starch/ maize stalk fiber boards	17.21	1917.81
The single layer jute fiber reinforced maize stalk fiber boards	20.26	1706.29
The dual layer jute fiber reinforced maize stalk fiber boards	23.17	2398.94
The first group of jute fiber hybrid reinforced maize stalk fiber boards	17.36	939.06
The second group of jute fiber hybrid reinforced maize stalk fiber boards	16.36	1768.11
The third group of jute fiber hybrid reinforced maize stalk fiber boards	16.21	1038.36

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4 Summary and conclusions

The following can be concluded from the research.

Physical models of fiber reinforced composites were established according to the microstructure analysis of the four species of insects’ elytra including *Protaetia orentalis*, *Copris ochus* Motschulsky, *Anoplophora chinensis* and *Cytister bengalensis* Aube.

The flexural strengths of the single layer jute fiber reinforced maize stalk fiber boards and the dual layer jute fiber reinforced maize stalk fiber boards were higher than those of the common maize stalk fiber boards and three groups of the jute fiber hybrid reinforced maize stalk fiber boards. Improvements in the flexural strength of the biomimetic boards were ascribed to the biomimetic design. The laminated biomimetic structures were proved to be superior to the hybrid biomimetic structures.

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