

## STUDY ON PREPARATION OF BAMBOO FIBER REINFORCED UNSATURATED POLYESTER RESIN "GREEN" COMPOSITES

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**ABSTRACT:** Composite materials are usually made with organic matrixes reinforced by synthetic fillers, such as carbon or glass fibers... . But the high cost and environmental awareness of the synthetic fibers has limited their application. Meanwhile, natural fibers have been very attractive because they have been low cost, low density, eco-friendly, available in high quantities, renewable, biodegradable and shown excellent mechanical properties. In this study, green composite materials were prepared by using unsaturated polyester resins and bamboo fibers. The fibers were previously modified by chemical treatment and inserted into matrix in the role of the reinforcement. Some factors effecting to properties of products, such as fiber content and modifier content were studied meticulously. As a result, composite products showed more advantages than neat polymer. For example, it does not only improve significantly mechanical properties but also becomes cheaper and friendlier with environment.

**Keywords:** bamboo fiber, "green" composite, unsaturated polyester.

### INTRODUCTION

Nowadays, polymer-matrix composites, such as carbon or glass fiber reinforced plastics (CFRP/GFRP) have been widely used in industry since they have high strength and modulus. When the thermosetting resins are used as a matrix, it is usually difficult to recycle the material. Wasted FRPs are almost damped although they do not decompose itself naturally in the ground, while others are burned. Energy recycling systems are also developed using polymer composites as solid fuel. However the glass fibers in composite reduce the net heat and might damage the

furnace, if their composite are burned in it as a solid fuel. It introduces another problem such as the disposal of the remains, because the glass fibers in the composite would also remain in the incinerator. For the past several years, public attention has gone to natural fibers as a resource due to their fast growth. Natural fibers are relatively inexpensive and easily available as renewable resource. In Vietnam, resources of natural fibers are very rich and multiform, such as wood fibers such as bamboo fibers, rice husk, coconut fibers, and cane fibers... This is promising to study about new green composites based on natural fibers with plastics to prepare

the new materials more friendly to environment [3-5].

There are many kinds of natural fibers exist on the earth, but only some of them have good characteristics to use as reinforcement in polymer composites [6]. They must have enough ability to improve mechanical properties of products.

## MATERIALS AND METHODS

### Materials

Luong bamboo plants were collected in Phu An Bamboo Park, Binh Duong, Vietnam. The Unsaturated Polyester resin SHCP 268 BQT having Styrene (St) concentration 30 %wt was from Singapore Highpolymer Chemical Products Pte Ltd, Singapore. Cross linking agent is Butanox M50 from Akzo Nobel (Asia) Co., Ltd, China. The commercial coupling agent Vinyl Silane (VS) (provided by Synatech Fine Chemicals Co., Ltd., China) was used in the role of the modifier to improve compatibility between matrix and reinforcement.

### Methods

#### *Fiber extraction*

The bamboo node portions and thin layer of exodermis and endodermis (bark) of the bamboo were removed. Rest of the hollow cylindrical portion of culm was taken for extracting fibers [7]. The cylindrical portion of the culms was peeled in the longitudinal direction to make strips of 1.0–3.0 mm thick, about 120-150 mm length and about 20-40 mm width. The strips were

bundled and immerse in the water for 72 hours to soften.

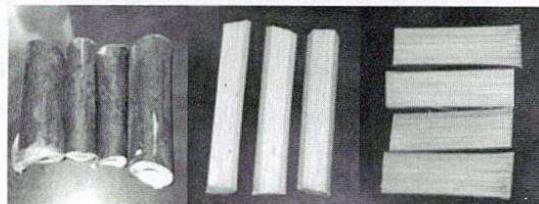


Figure 1. Some pictures of Bamboo parts

Conventional method, roller mill technique (RMT) was explored for the mechanical separation [8]. Bamboo strips were executed in two stages according to parallel directions compared to axis. The first stage, trips were rolled preliminarily a time. During this time, distance of two axes was 0.5 mm and axis rate was 60 cycles per minute. Second stage, axes were adjusted to 0.1 mm distance and then strips were rolled two times.

#### *Examine size distribution of fibers*

After fibers were separated, they were exposed to the sun in 48 hours and then dried in 72 hours at 80°C to remove remaining water. To examine the length of fibers, 10 gram of bamboo fibers was weighed by an analytical balance. We pulled out each fiber and observed length of them. And then we calculated number of the fibers distributing in each long range.

#### *Preparation of modified bamboo fiber mat*

Fibers having length distribution 1-2.5 cm were weighed exactly 10g. They were scattered on mould with dimension 170 mm x 170 mm

length and width. After that mould was pressed under pressure 60 bars at temperature 120°C in 30 seconds to prepare the mat about 0.3 mm thickness.

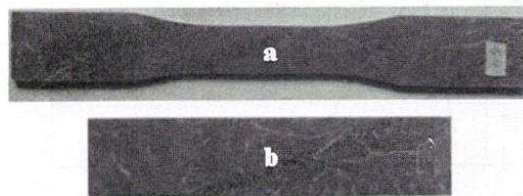
To overlay coupling agents on the surface fibers, VS was dissolved into solvent mixture Water: Ethanol and solution was maintained at pH = 4 by Acetic acid. Solution of coupling agent was prepared at many different concentrations 0.3, 0.5, 0.7, 0.9 %wt. After that it was sprayed on two surfaces of mats and then mats were given in oven at 70°C in 12 hours. During this time, etherification reaction happens between fiber surface and coupling agent.

#### *Preparation of composite material samples*

The composite sheets having size 17 cm x 17 cm x 0.2 cm length, width and thickness respectively were made by hand lay-up method according to following processing conditions. The selective mat layers were poured with suitable quality of UPR. The wetted fibre mat layers were superposed each other in the mould and then placed between the heating platens of a press at 80°C. The mould was heated to 120°C under pressure of 60 bars. And then it was remained in 45 minutes to define shape of the samples. Finally, samples are taken out and go through the post-cure process in an oven at 80°C in 24 hours.

#### **Measurements**

Mechanical properties, such as: tensile strength and flexural strength were tested according to ASTM standard D 638 (Figure 2a) and D 790 (Figure 2b) respectively. Flexural strength was performed using three-point bend tests with span to depth ratio of 16:1. Specimen like dog bone of tensile test and specimen of flexural test were measured and recorded the width and thickness. Samples were tested at a crosshead speed of 1 mm/min by a Comotech machine (Taiwan). The achieved results modulus and stress were calculated from these tests.



**Figure 2.** Shapes of samples according to ASTM standards D 638 and D 790

Adsorbent spectrums of treated and untreated fibre surfaces were taken using a FTIR spectrometer Tensor (Germany) using the KBr disc. Scans were taken with a resolution of 2 cm<sup>-1</sup>.

The degree of crystallinity of the untreated and treated of fibers was displayed from X-ray diffractograms of a Shimadzu X-ray diffractometer (Japan) with Ni filtered CuK<sub>α</sub> radiation of wavelength 1.5417 Å at 40 kV and 30 mA.

SEM micrographs at broken surfaces of composites with treated and untreated fibre were taken using a scanning electron microscope Model JSM-6600 (Japan).

## RESULTS AND DISCUSSION

### Characteristics of Luong bamboo fibers

#### *Effect of extraction technique on distribution of fiber length*

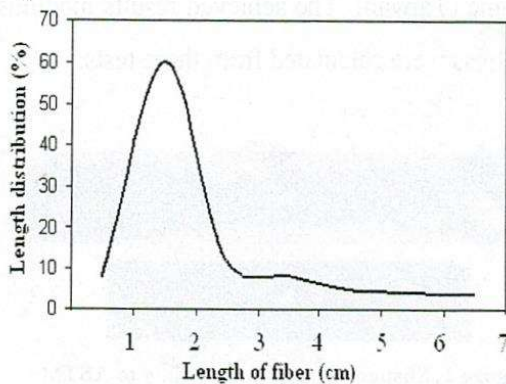


Figure 3. Length distribution of bamboo fibers

The distribution of fiber length after separated by a mill rolling machine was shown in the Figure 3. The results expressed that fiber length distribution mainly concentrated in range 1-2.5 cm (Figure 4). The small size of BFs could help to increase surface area contacting between fiber surface and matrix.

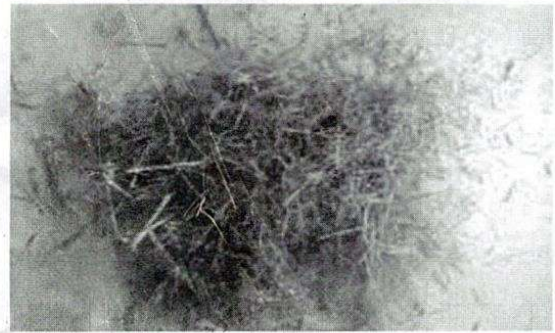


Figure 4. Bamboo fibers extracted by RMT method

Achieved results could be understood through mechanism of fiber separation of RMT. Strips were simultaneously influenced by both tearing and press stress along each fiber bundle, and then bundles were cleaved but not were broken off. Generally, RMT was suitable to separate fiber for preparing composite material because it could produce fibers having quite homogeneous length and small diameter [8, 10].

#### *Effects of alkali treatment on structure of the BFs*

Generally, structure of BFs like other natural fibers, is composed of some main components, such as cellulose, hemi cellulose, lignin, a little amount of other organics, such as xylem, pentosan, wax, pectin and inorganic minerals [9]. Hemicellulose differs from cellulose in three important aspects. For example, it contains several different sugar units, exhibits a considerable degree of chain branching and has the degree of polymerization of hemicellulose ten to one hundred times lower than that of native cellulose [10]. Lignins are amorphous, highly

complex, mainly aromatic, polymers of phenylpropane units distributing throughout the secondary cell of fiber as a cell wall adhesive<sup>5</sup>. These ingredients cover cellulose part and obstruct interaction between cellulose and resin in composite. That strongly affects to properties of composite materials.

Result of FT-IR spectrum of treated BFs was shown in figure 5b. The peak appearing at 3200-3500  $\text{cm}^{-1}$  is specific vibration of the hydroxyl groups of cellulose virtually does not change before and after fibers are treated. Meanwhile, particular peak of C=O vibration of hemi cellulose at 1740  $\text{cm}^{-1}$  is almost disappeared. In addition to, the peak intensity of symmetric vibration of CH<sub>3</sub>-O- groups of lignin at 1250  $\text{cm}^{-1}$  is much reduced. On the other hand, a decrease of intensity at 840  $\text{cm}^{-1}$  position of  $\beta$ -glucosidic bonds existing in structure of polysaccharides is also displayed. In short, the 1% NaOH treatment essentially removed significant amount of hemi cellulose, a little of lignin and other polysaccharides... [12] from fiber structure.

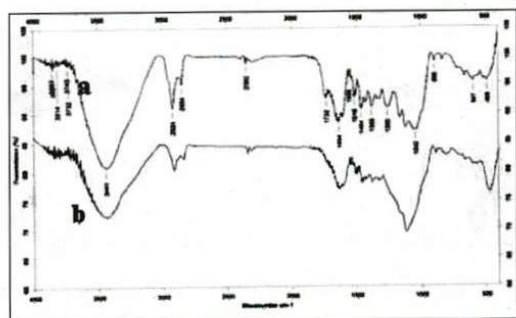


Figure 5. FT-IR spectrum of (a) untreated fiber and (b) 1% NaOH treated fiber in 72 hours

The effect of fiber surface by NaOH treatment was proved in Figure 6. Surface of BFs was taken by a Dino optical microscope having enlargement range 200 times. Figure 6a showed surface of BFs before treated. We could see lignin and something like that overlay around cellulose part. Nevertheless, after fibers were treated (Figure 6b), surface became more clean and glib. That demonstrated ingredients, such as hemi cellulose, lignin... were removed considerably.

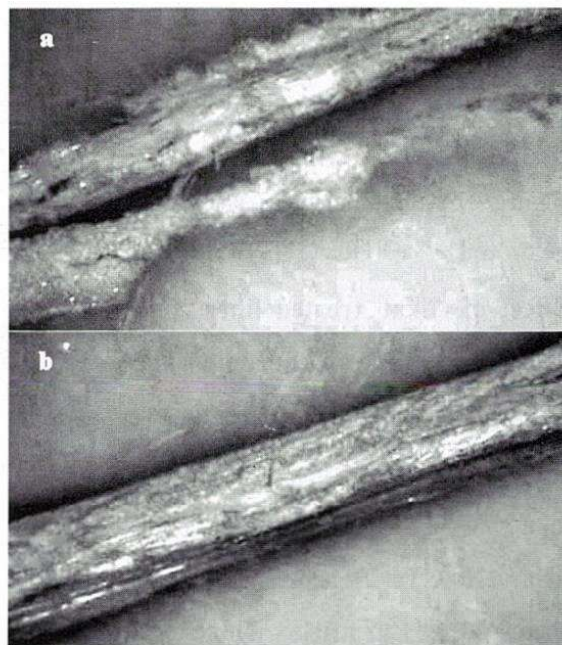


Figure 6. Micrographs of longitudinal views of (a) untreated fiber and (b) 1% NaOH treated fiber.

Besides, NaOH treatment process also affected to crystallization of fibers (Figure 7). Because of removing hemi cellulose, lignin and others made structure of BFs become get loose,

so crystallization content decreased slightly. Hydroxyl groups of cellulose became more flexible and they could be easier to bond to functional groups of coupling agents. As a result, this make fiber surface had good ability to adhere with organic matrix.

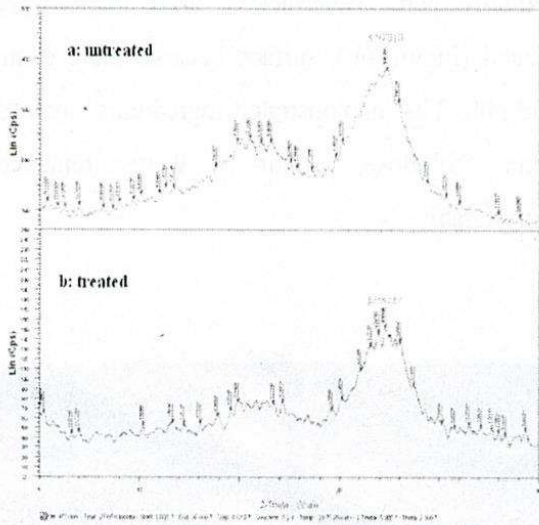


Figure 7. Crystallization of (a) untreated fiber and (b) 1% NaOH treated fiber in 72 hours

**Effect of Alkali treated fiber content on the mechanical properties of composites**

From Figure 8, when fiber content increased, both tensile stress and tensile modulus were improved and obtained maximum value at 90phr fibers. However, tensile strength of composite decreased at 110phr fibers. These results could be explained that UPR was not enough to completely dampen on the surface of BFs at high loading of fibers. So that this phenomenon caused tensile properties of products to decrease.

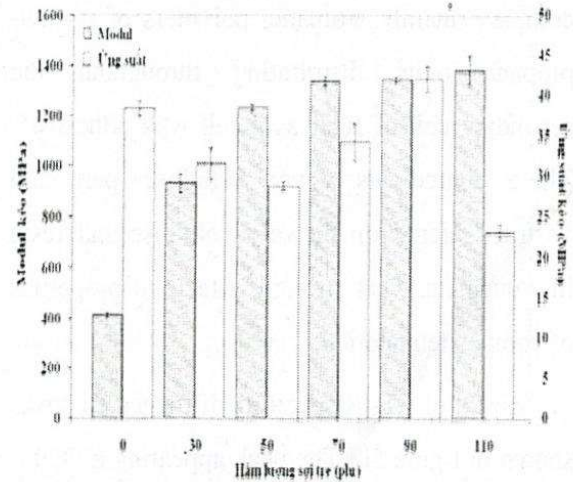


Figure 8. Effect of 1% NaOH treated fiber content on the tensile strength of composites

Flexural strength of composite also showed like tensile strength (Figure 9). When fiber content increased, the flexural strength increased too. Flexural modulus gained maximum value at 90phr fibers and then lowered at 110phr fibers. Flexural tensile also gained the best at 70phr fibers and almost only reduced slightly at 90phr fibers.

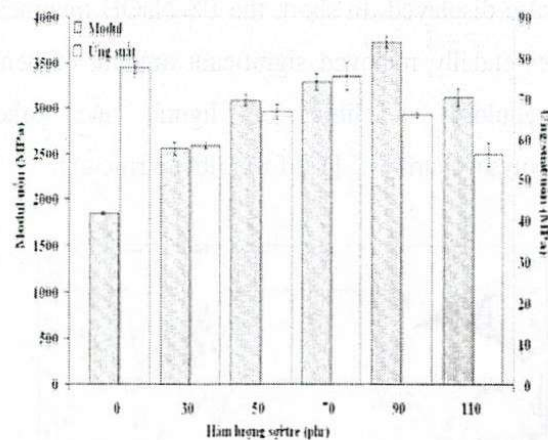


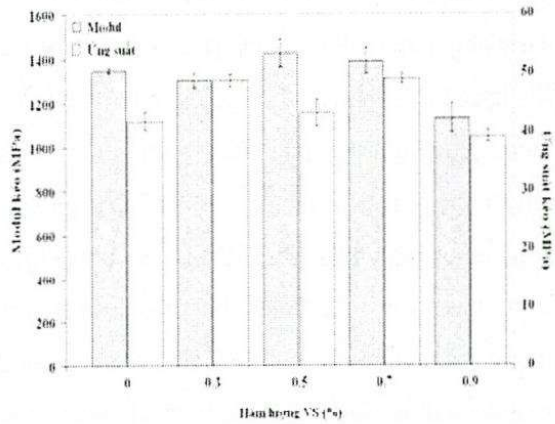
Figure 9. Effect of 1% NaOH treated fiber content on the flexural strength of composites

Through results, such as tensile strength and flexural strength, the suitable fiber content

applied for preparing composite products was 90phr.

**Effect of coupling agents on mechanical properties of composite materials**

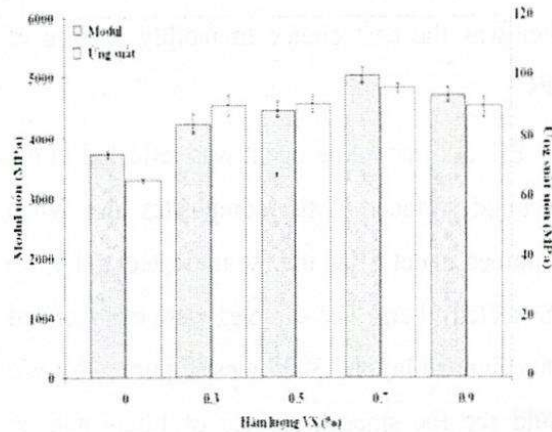
The coupling agent was used to improve compatibility between fibers and UPR. Figure 10 shows the effect of coupling agent on tensile strength of composites. VS executed good ability to connect two main phases in composite. Tensile strength displayed that properties of composites are enhanced considerably at 0.7%wt VS. Tensile modulus and tensile stress increased 6%, 18.7% respectively.



**Figure 10.** Effect of VS content on the tensile strength of composites

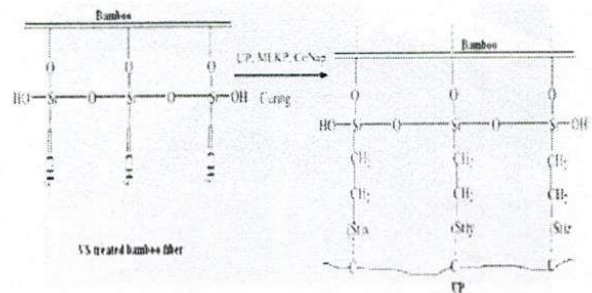
From Figure 11, flexural strength also displayed an betterment when VS was used. The flexural stress and modulus also increased according to coupling agent content. Flexural strength was meliorated when VS content increased from 0.30 to 0.70%wt. This property diminished at 0.90%wt VS, but it were still better than composites that did not use VS at the

same fiber content. Flexural strength gained maximum values at 0.7%wt VS and the flexural stress and flexural modulus were as high as 35%, 46.8% respectively.



**Figure 11.** Effect of coupling agent content on the flexural strength of composites

The improvement of mechanical properties could be explained by following mechanisms (Figure 12).



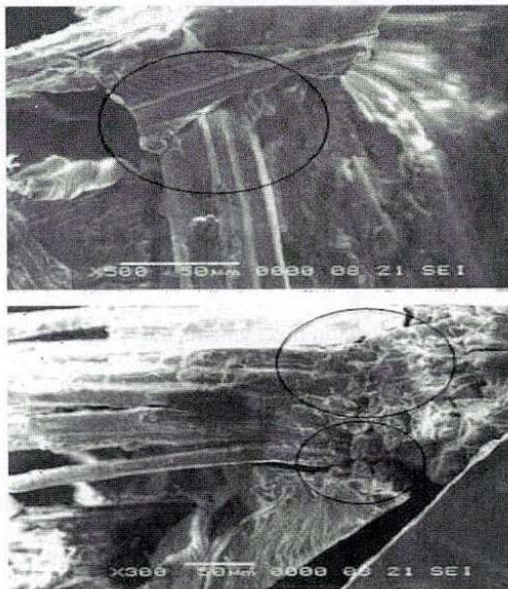
**Figure 12.** Adhesion mechanisms between matrix and fibers when using coupling agents VS.

Structure of VS contained two kinds of functional groups hydroxyl groups and vinyl groups. Of course, these hydroxyl groups would react to hydroxyl groups of fibers through etherification and vinyl groups would participate in cross linking process of UPR. As a result, the

coupling agents became good chemical bridges to connect between organic matrix and filler.

Summarizingly, from mechanical properties of composite sheets reinforced by three kinds of chemical treated BFs showed that VS treated fiber was the best choice to modify surface of BFs.

Effect of coupling agent was reflected in the fractured surfaces of the composites also when examined under SEM in case untreated and 0.7% VS treated fibers. The samples were exaggerated 500 (Figure 13a) and 300 times (Figure 13b). We could see the smooth surface of fibers and an obvious distinguishing between fiber surface and matrix in composites made from VS untreated fibers. It demonstrated that there was not good compatibility between these two phases.



**Figure 13.** SEM of composite samples having 90phr fibers: (a) untreated fibers; (b) 0.7% VS treated fibers.

However, when VS was used to modify fiber surface at 0.7%wt, composite showed that VS treated fibers and UPR well compatibilized together (Figure 13b). Rough surface of BFs could be cause by VS bridges connecting fibers and matrix. Treatment process through VS helped to improve surface of fibers becoming more hydrophobic and made the chemical linkages between fibers and resin through covalent bonds. Therefore, mechanical properties of composite materials were increased.

## CONCLUSION

In Vietnam, bamboo is very variety and multiform, so applications based on this kind of material is required. Cost and fiber strength of the BFs have been shown more excellently than other fibers. Low density and high strength of BFs prove to be attractive factors for the fabrication of lightweight materials. The RMT was concerned as the best way to extract fibers because it was simple method and achieved fibers were long enough and uniform. Through mechanical and chemical treatment processes, the fibers derived from Luong bamboo showed very well when they were used to reinforce in composites at content 90phr. Especially, when VS was used to modify surface of BFs at content 0.7 %wt respectively, mechanical properties were improved so much.



## NGHIÊN CỨU CHẾ TẠO COMPOSITE “XANH” TRÊN CƠ SỞ NHỰA POLYESTER KHÔNG NO GIA CƯỜNG BẰNG SỢI TRE

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**TÓM TẮT:** *Vật liệu composite thông thường được chế tạo từ nhựa nền hữu cơ gia cường bằng các loại sợi tổng hợp, như sợi cacbon, sợi thủy tinh... Nhưng nhược điểm của loại pha gia cường này là giá thành cao. Trong khi đó sợi tự nhiên là nguồn tài nguyên đang rất hấp dẫn vì chúng có giá thành thấp, tỉ trọng thấp và có khả năng tái tạo. Trong nghiên cứu này chúng tôi tiến hành nghiên cứu chế tạo composite “xanh” trên nền nhựa polyester không no và sợi tre. Sợi được xử lý hóa học và đưa vào nhựa nền với vai trò là pha gia cường. Các thông số ảnh hưởng đến tính chất cơ lý của sản phẩm như hàm lượng sợi tre, hàm lượng chất trợ tương hợp cũng được khảo sát. Kết quả cho thấy vật liệu composite có nhiều ưu điểm hơn so với polymer nền ban đầu. Sản phẩm tạo thành không những có tính chất cơ lý được cải thiện khá tốt mà còn có giá thành rẻ hơn và thân thiện hơn với môi trường.*

**Từ khóa:** *composite “xanh”, sợi tre, nhựa polyester không no.*

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