

Effect of nanoclay on properties of the biocomposite based on unsaturated polyester resin and bamboo fibers

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Received 12 September 2011, received in revised form 30 September 2011

Abstract. Recent times, composite materials based on organic matrixes were reinforced by natural fibers have been attracting many researches [1,2,3]. Because natural fibers have been very attractive, such as low cost, low density, eco-friendly, available in high quantities, renewable, biodegradable and shown excellent mechanical properties [4]. And since natural fibers were used as a filler in composites, products were not only improved physical mechanical properties but also cheaper and friendlier with environment. However, researchers reported on biocomposites made from polyester resin, natural fibers and nanoclay have been rather limited.

In this study, biocomposite was prepared by using Unsaturated Polyester resins (UP), bamboo fibers (BFs) and nanoclay. Fibers separated from bamboo body by mechanical method had size distribution mainly between 0.24 - 0.40 mm diameter and 1- 2.5 cm length. Fibers were treated by Sodium Hydroxide and coupling agent Vinyl Silane to help improve compatibility between fibers and polymer matrix. The biocomposites from Unsaturated Polyester resins and modified fibers were prepared by Hand lay up method. The first, nanocomposite materials from UP and nanoclay were prepared by solution method. After that solution was poured on to the selective mat layers. The wetted fibre mat layers were superposed each other in the mould and pressed in two heated platens at 120°C to prepare composites. The effects of factors on properties of materials, such as concentration of coupling agent and loading of modified clay...were studied meticulously. As a result, composite products showed good properties at 90phr of bamboo fibers modified by Vinyl Silane solution 0.7% and 1phr of nanoclay filler.

Keywords: Bamboo fiber, composite, polymer, Unsaturated Polyester, nanoclay.

1. Introduction

Nowadays, thermosetting are being used widely on the world in many fields because of many advantages, such as: high temperature strength and well resisting abrasion, chemicals, UV and water...

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but they also have some weakness. For example, they could not be recycled and a large loading of monomer Styrene used as a diluent to reduce the viscosity of UP badly effects to workers and environment during cross-linking process. So studying about composites based on fibers and thermosetting not only helps to improve properties of material but also reduces significantly using content of thermosetting as well as monomer. For a long time, composites based on synthetic fibers have been studied and extensively utilized in commercialism. But the high cost and environmental awareness of the synthetic fibers has limited their application [5]. Meanwhile, natural fibers are relatively inexpensive and an easily available renewable resource and sources of natural fibers are very rich and multiform, such as wood fibers, bamboo fibers, rice husk, coconut fibers, and cane fibers....That promises to study about new biocomposites based on natural fibers with plastics to prepare the new materials more friendly to environment [6, 7,8].

The aim of the present work involves to the preparation of biocomposite materials by using bamboo fibers as reinforcement for UP matrix and added nanoclay. The application of natural fibers as reinforcement in composite materials requires a strong adhesion between the fibers and the synthetic matrix because the macroscopic mechanical properties depend on the fiber-matrix interface. To make good use of bamboo fiber reinforcement in composites, Vinyl Silane treatment was applied to optimize interface and to promote adhesion. Structure and properties of biocomposite materials were characterized by some techniques, such as Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscopy (SEM), flexural and tensile tests and thermo gravimetric analysis....

2. Experimental methods

2.1 Materials

Luong bamboo plants were collected in Phu An Bamboo Park, Binh Duong province, Vietnam. Unsaturated Polyester SHCP 268 BQT having Styrene concentration 30%wt was from Highpolymer Chemical Products Pte Ltd, Singapore. Cross-linking agent is Methyl Ethyl Ketone Peroxide (Butanox M50) from Asia Akzo Nobel Co., Ltd, China. Vinyl Trimethoxy Silane (Silquest silane A-171) was provided by Synatech Fine Chemicals Co., Ltd., China. Motmorillonite N757 was provided by 4 Sud. Chemie. Corporation, Germany.

2.2 Experiment

2.2.1 Preparation of modified bamboo fiber mat

The bamboo fibers (BFs) separated from strips was treated by 1%wt NaOH solution in 72 hours. After that solution was neutralized by Sodium Carbonate to pH=7. Fibers were taken out and washed many times by water. Continuously, they were dried in oven at 100⁰C in 3 hours. After that, 10 gram of fibers were scattered on mould measuring 170 mm x 170 mm length and width. Mould was pressed at 120⁰C, p= 60 bar in 30 seconds to prepare the mat having 0.3 mm thickness. To overlay coupling agents on the surface fibers, VS was dissolved into solvent system Water: Ethanol (5:95) and solution

was maintained at $\text{pH} = 4$ by Acetic acid to make the hydrolysis occurs. Solution of coupling agent was sprayed on two surfaces of mats. Mats were then pressed hot at 110°C in 3 minutes and then stored in a vacuum oven at 80°C .

2.2.2 Preparation of composite material samples

From previous researches, we have demonstrated that mechanical properties of composite were best improved at loading of NaOH treated fiber 90phr [9]. Therefore, in this study, we investigated effect of coupling agent Vinyl Silane and nanoclay through this loading.

The composite sheets having size 17 cm x 17 cm x 0.2 cm length, width and thickness were made by Hand lay-up method. Montmorillonite was modified by PEO according to melting method. Author Zhiqi Shen had demonstrated saturation ratio close to 30 mass % for PEO intercalated into MMT, so the ratio of PEO/MMT 3/10 was chosen [10]. The nanocomposite was prepared by mixing UP and nanoclay with varying contents of nanoclay, such as 1, 3, and 5phr. Mixture was stirred in a vessel in 6 hours at 80°C . After that 1% wt initiator was added and continued stirring in 1 minute. Finally, solution was either poured into suitable mould to cure at 80°C and followed by post curing at 120°C in 45 minutes or used to coat onto mat layer to prepare biocomposite.

The selective mat layers were poured with an enough suitable quality of UP. The wetted fibre mat layers were superposed each other in the mould and then placed between the electrically heated platens of a hot press at 80°C . The mould was heated to 110°C at a molding pressure of 60 bars. And then it was remained in 20 minutes to define shape of the samples. Finally, samples were taken out and went through post-cure process in an oven at 80°C in 24 hours.

3. Results and discussion

3.1 Effect of coupling agent Vinyl Silane on morphology and mechanical properties of composites

Figure 1 shows effect of Vinyl Silane on mechanical properties of composites at 90phr fibers. VS executed good ability to connect two main phases in composites. When compared to samples with VS untreated 90phr fiber, tensile strength of these samples displayed better and enhanced considerably at 0.7%wt VS with tensile stress increased 17%. Meanwhile, flexural strength also displayed 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 0.3 to 0.7%wt and it gained maximum values at 0.7%wt VS with flexural modulus and stress increased 35 and 47%, respectively .

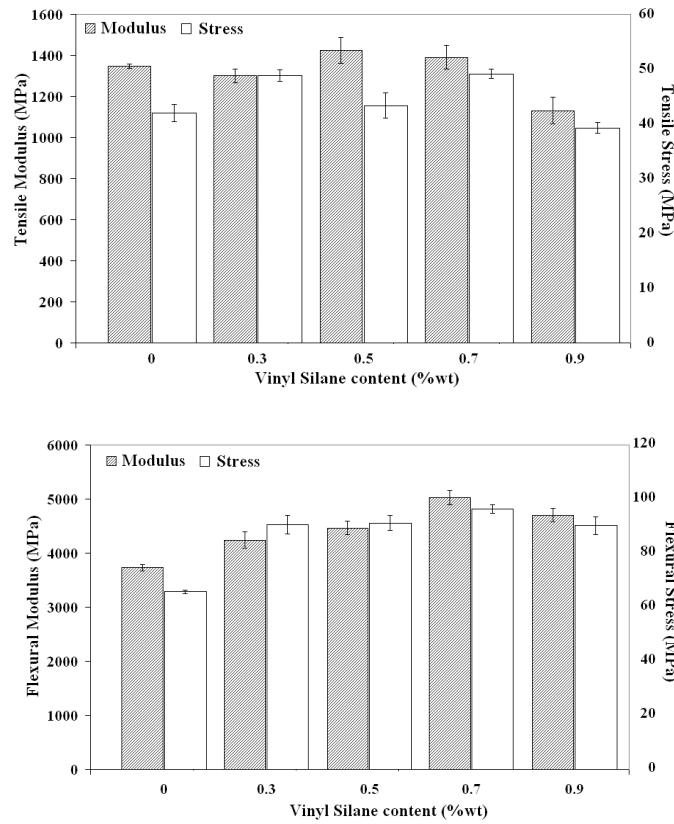


Figure 1. Effect of Vinyl Silane content on the mechanical properties of composite UP/BFs (100/90) products

The improvement of mechanical properties when coupling agent was used, could be explained by following mechanisms (figure 2)

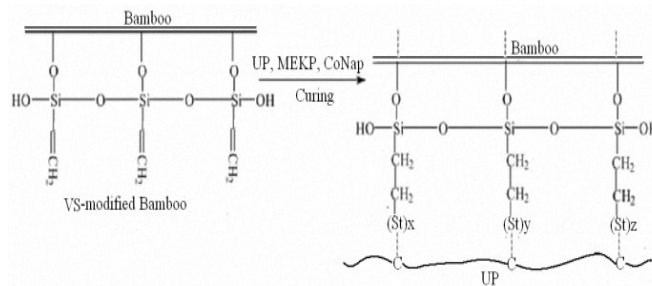


Figure 2 Adhesion mechanisms between matrix and fibers when using coupling agents VS

Structure of VS contained functional groups, such as hydroxyl and vinyl groups. In acidic environment, these groups would react to hydroxyl groups of fibers through etherification processing. From there, coupling agent was grafted on the structure of bamboo fibers and that made fibers become more hydrophobic. On the other hand, vinyl groups existing on structure of coupling agent would also

participate in cross-linking process of UP. As a result, coupling agents became good chemical bridges to connect organic matrix with filler.

Figure 3 shows result of FT-IR spectrum of BFs. The peak appearing at range 3200-3500 cm^{-1} was specific vibration of the hydroxyl groups of cellulose virtually did not change before and after fibers were treated by NaOH (Figure 3a and b). When fibers were treated by NaOH, particular peak of C=O vibration of hemicellulose at 1732 cm^{-1} was almost disappeared (Figure 3b). Meanwhile, the peak intensity of symmetric vibration of $\text{CH}_3\text{-O-}$ groups of lignin at 1250 cm^{-1} was much reduced. In short, the 1% NaOH treatment essentially removed significant amount of hemicellulose, a little of lignin from fiber structure.

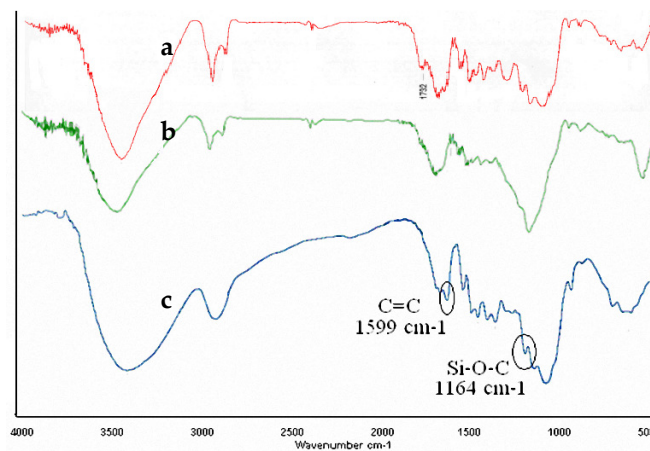


Figure 3. FT-IR spectrum of (a) untreated fiber and (b) 1% NaOH treated fiber in 72 hours, (c) 0.7% VS modified fiber.

After fibers were modified by VS 0.7% they were soaked in Ethanol solvent Acetone to remove amount of unreacted VS by Soxhlet processing in 15 hours. Inspection of Figure 3c shows appearance in absorption of peak at 1599 cm^{-1} and 1164 cm^{-1} after modifying process of fibers. These were characteristic vibrations of the C=C and Si-O-C bonds, respectively. This demonstrated the reaction of OH groups from VS with OH sites along cellulose chains to create chemical bonds.

Effect of coupling agent was reflected in the fractured surfaces of the composites when materials were examined under SEM in case untreated and 7% VS treated fibers in figure 4. We could see the smooth surface of fibers and an obvious distinguishing between fiber surface and matrix in composites made from VS untreated fibers (figure 4a). It demonstrated that there was not good compatibility between these two phases.

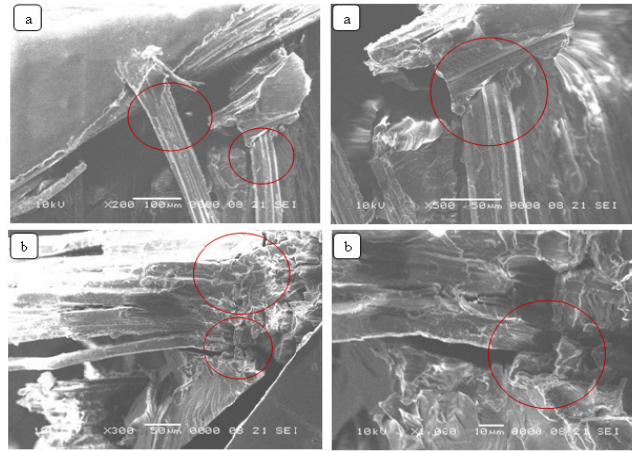


Figure 4. SEM of composite samples having 90phr fibers: (a) untreated fibers; (b) 7% VS treated fibers

However, when VS was used to modify fiber surface at 7% VS, composite showed that VS treated fibers and UP well compatibilized together (figure 4b). 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, properties of composite materials were notably improved.

3.2 Effect of nanoclay on properties of composites UP/0.7% VS treated bamboo fibers (100/90)

3.2.1 Effect of nanoclay on Mechanical property

The figure 5 shows the mechanical properties of materials with existing of nanoclay. In nanocomposites (B, C and D), when nanoclay was used to reinforce neat resin system, tensile strength of materials increased considerably and obtained the best value at 1phr nanoclay.. Since 1phr nanoclay was filled into composite system based on UP and 90phr BFs treated by 0.7% VS, modulus and tensile stress were also improved slightly. The same results were also obtained in flexural strength but it increased quite impressionably. Flexural modulus and stress of composite added 1phr nanoclay were increased 8% and 6%, respectively when compared to E sample.

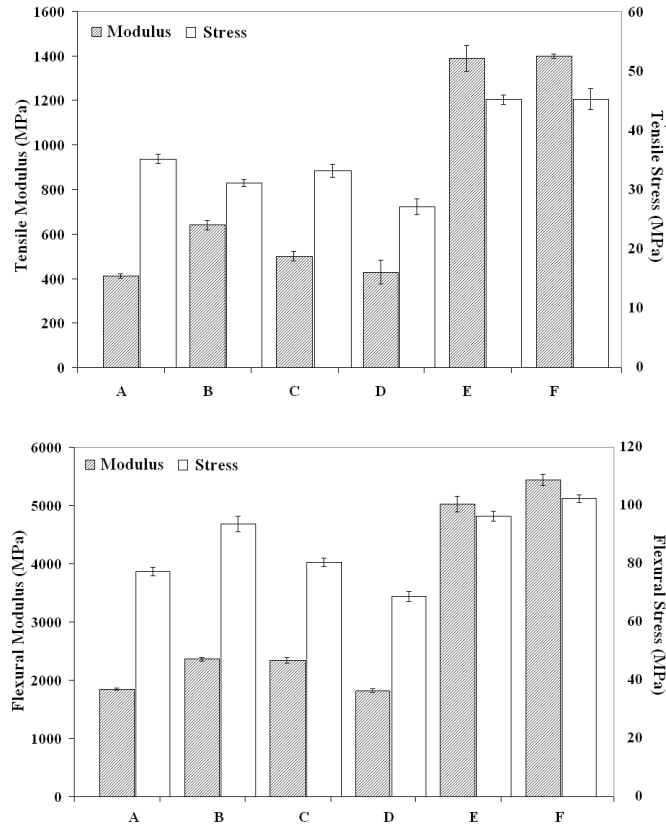


Figure 5 The mechanical properties of products: (A) neat UP; (B) UP/1pbr nanoclay; (C) UP/3pbr nanoclay; (D) UP/5pbr nanoclay; (E) UPR/ 90pbr BFs modified by 0.7% VS; (F) UP/ 90pbr BFs modified by 0.7% VS /1pbr nanoclay.

3.2.2 Effect of nanoclay on thermal property

Biocomposite samples were tested at heating rate 20⁰C/min from 0-600⁰C (Figure 6). Degradation temperatures of composites in E and F were lower than of neat resin A and nanocomposites B. The existing of 90pbr fibers in structure of composite caused degradation temperature of E and F samples decreased considerably and made degradation process of composite differed from A and B samples. When nanoclay was added into composite materials, it helped improved not only mechanical properties but also thermal property. For example, onset degradation temperature, first maximum degradation temperature and second maximum degradation temperature of F sample using nanoclay at 1pbr increased 8.5⁰C, 7.5 and 1⁰C respectively when compared to E sample without nanoclay. Generally, onset degradation temperatures and maximum degradation temperatures were improved slightly when nanoclay was used to reinforce in composite materials.

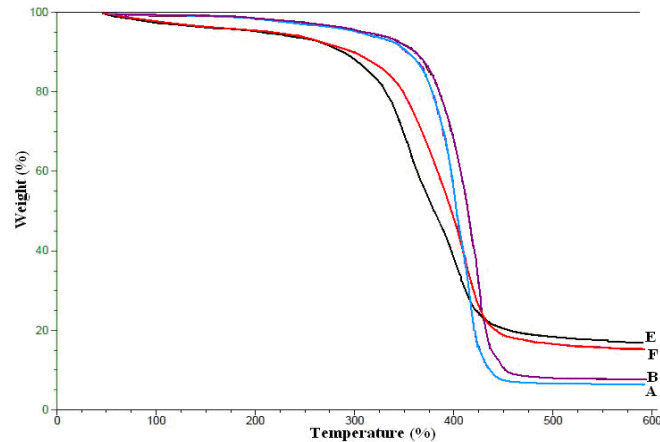


Figure 6. Curves of Thermo gravimetric analysis (TGA) for samples: (A) neat UP; (B) UP/1phr nanoclay; (E) UPR/ 90phr BF modified by 0.7% VS; (F) UP/ 90phr BF modified by 0.7% VS /1phr nanoclay.

3.2.3 Effect of nanoclay on water adsorption

Summarizingly, water adsorption of all composites was higher than neat UP (Figure 7). These results were caused by hydrophilic property of fibers existing in resin system. Free hydroxyl groups of fibers interacted with water molecules through hydrogen bonding, adsorbed and kept water molecules into structure of composite materials. We could obviously see increasement of water content in UP/ 90phr unmodified fibers composite (A2). When VS was used in the role of the coupling agent to connect fibers and polymer matrix, the reactions took place between VS and fiber surface like in figure 2 making increase in the compatibility between fibers and polymer matrix and UP covered around surface of fiber. From there it well improved hydrophilic property of fibers. That was the reason to explain why the water uptake of material lowered remarkably. When nanoclay was used in the role of reinforcement, it also helped material to resist water better (A4). This resulted from dispersing of modified MMT into polymer to create homogeneous structure of nanocomposite. And MMT layers crept into slits of material and obstructed the penetration of water. Only 1phr nanoclay was filled into composite, it not only increased mechanical properties but also made water adsorption ability decreased noticeably when compared to other composite samples.

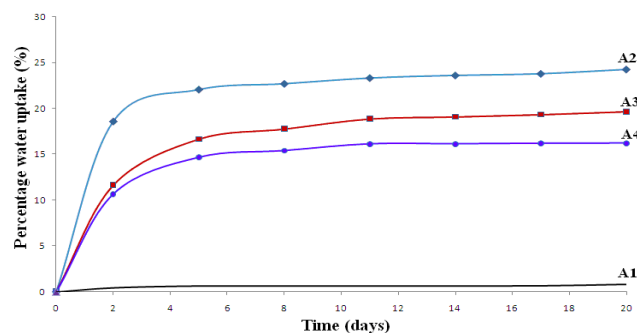


Figure 7. Water uptake of neat UPR and composite samples: (A1) neat UP; (A2) UP/ 90phr unmodified BF; (A3) UPR/ 90phr BF modified by 0.7% VS; (A4) UP/ 90phr BF modified by 0.7% VS /1phr nanoclay.

4. Conclusion

Biocomposite has been one of new trends in material field in recent time. Especially, material from natural fibers and polymer matrix attracts many researches to prepare the composite having good mechanical properties, lightweight, friendly to environment and low cost... In Vietnam, bamboo is very variety and multiform, cost and fiber strength of the BFs have been shown more excellently, so composite material based on bamboo fiber promises many potential applications in future. Through 0.7% VS treatment, fibers were used to reinforce in composites, the products showed very well. Besides, nanoclay also displayed good ability to improve properties of composite since it was used in the role of reinforcement to fill into polymer matrix at 1phr. As a result, mechanical properties, thermal property and water resistance of material were increased considerably.

Acknowledgements. The study supported by a grant from the Department of Material Science, Ho Chi Minh University of Science. We thank all participants for their enthusiasm and cooperation in the study.

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