

Preparation of Natural Fiber Kenaf Composite and Its Properties through Graft Polymerization Method

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Abstract

The present study is aiming to find the optimal condition of methyl methacrylate (MMA) graft polymerization onto natural kenaf fiber and exploring the use of grafted kenaf fiber in PMMA-based thermoplastic composite. The results of the study show that the effect of pretreatment time, the important of cerium concentration and the role of the reaction time are significantly affect the graft yield of MMA monomer onto kenaf fiber in a positive trend. This graft polymerization technique was intended to be used to alter hydrophilic feature of natural kenaf fiber in order to increase the compatibility with the polymer matrix material. In order to examine the applicability of the grafted kenaf as the reinforcement of composite material, the grafted kenaf with graft yield of ca. 160 % was prepared in a large-scale experiment. The grafted kenaf fiber and PMMA powder were dry-blended so the mixture contains 60 wt% PMMA in total composition and have molded into composite plates by hot-pressing method. The composite plate with using untreated kenaf fiber was also prepared for the comparison. The essential characteristic of the composites such as mechanical properties and water absorbency were evaluated. Confirmation of the improved interfacial adhesion between the fiber and the matrix was also discussed. From these results, it could be concluded that the modification of natural kenaf fiber by graft polymerization method can effectively improve the poor adhesion between PMMA matrix and kenaf fiber and provide better characteristics of the natural fiber based composite material.

Keywords: Natural kenaf fiber, graft polymerization, mechanical properties, kenaf composite

I. Introduction

Recently, plant-based natural fibers have received a great deal of attention as potential fillers or reinforcement in the area of developing newer composites that have both economic and environmental benefits. The promising fiber sources that are being looked seriously are agricultural plant sources and fast-growing crops such as kenaf (*hibiscus cannabinus L.*). Kenaf has been identified as a viable non-wood plant source of industrial fiber for pulp and paper [1,2] as well as reinforcement for plastic composite owing to its characteristic of high strength to weight ratio, low density, low cost, recyclability and biodegradability as natural fiber [3]. In addition, as a source of plant that can be harvested in four to five months, kenaf has become a potential environmental friendly resource to absorb as much as carbon dioxide from the atmosphere to prevent the global warming [4,5]. Therefore, it has been a challenging for industrial practitioner to contribute in preventing the global warning by finding the way of applying natural fiber such as kenaf to be used for their products. One of the commonly used product is a composite, which is a combination product of natural kenaf fiber mixed with the polymer matrix. However, using kenaf fiber as reinforcement in composite will face the lack of compatibility to the matrix due to its nature of hydrophilic properties. Consequently, the interfacial adhesion problem between the two components of the composite limits the applicability kenaf into the direct mixing with the matrix. Therefore, modification technique is needed to finally solve the compatible adhesion problem by altering the hydrophilic surface property of the kenaf.

Graft polymerization is the technique used in the present study prior to composite preparation because it is very useful method in modifying the chemical and physical properties of natural and synthetic fiber, yielding a desirable product. Graft polymerization of vinyl monomer onto natural fiber has been accomplished by using initiators to generate free radical under thermal or photo-irradiation condition [6-9]. From the various initiators, ceric ion has been used extensively in effecting the graft polymerization of a variety of vinyl monomers onto cellulosic fiber or cellulosic substrates because of offering a particular advantage for the possibility of eliminating the large amounts of homopolymers [10], which are usually formed during grafting process.

The present study is aiming at realizing the optimum condition for graft polymerization of methyl methacrylate (MMA) onto natural kenaf fibers, and exploring the use of grafted kenaf fiber in PMMA-based thermoplastic composites. Graft polymerization provides an effective method for modifying the surface of natural fiber and enhancing its performance, yielding improvement of the interaction and adhesion between the fiber and polymer matrix, thus, it will increase the mechanical properties of fiber composites.

II. Experimental

2.1. Material

The kenaf fiber used was produced in Anhui Province, China and supplied by Uni Corporation, Japan. The fibers were obtained from the bast of kenaf plant and about 5

mm in length. The fibers were simply washed with boiling water and then dried before the following graft-polymerization experiments. Ammonium cerium nitrate used as an initiator and methyl methacrylate monomer were obtained from Wako Pure Chemical Ltd. The MMA monomer was distilled under reduced pressure before used. Ammonium cerium nitrate was used without further purification, and was dissolved in 0.1 M nitric acid. PMMA ($M_w = 725000$) powder was used as matrix material for preparing kenaf composite. Other chemicals and solvent were used as received.

2.2. Graft Polymerization

At room temperature, a given amount of kenaf and the cerium solution ($(\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ in 0.1 M HNO_3 aq.) were immersed in a pyrex glass tube, as the pretreatment technique. After a certain immersed time, MMA monomer was poured into the tube. Afterward, the reaction tube was deaerated, while at the same time the system was flushed in with nitrogen. The tube was then kept in a constant temperature water bath and maintained at 50°C to perform graft polymerization. After a period of reaction time, the grafted material was filtered, and then was extracted with THF for 24 hr to remove the homopolymers. The grafted material was then dried in an oven until constant weight was obtained prior to grafting value measurement. The optimal graft condition will be used to prepare grafted kenaf in large-scale experiments for composite preparation. For the purpose of grafting confirmation, SEM observation and FTIR analysis will be conducted.

2.3. Composite Preparation

9.63 gr of grafted kenaf fiber (PMMA content 62% wt) and 3.25 gr PMMA powder (in total, kenaf : PMMA = 40 : 60 (wt : wt)) were initially put into the molding frame (ca. 10×10 cm) and heated at 180°C without applying pressure for 1 min. Pressure of 100 kg/cm^2 at the same temperature was carried out for 5 min afterwards. Finally, with inserting the 3 mm thick plate into the frame at the same pressure, the temperature was increased to 200°C to press the material for another 10 min to give about 1.2 mm thick plate. The as-prepared composite was slowly cooled then to the room temperature by keeping the pressure. As comparison, the chemically untreated kenaf composite was also prepared at the same kenaf content in the similar conditions as the grafted kenaf sample to give a result in 1.15 mm thick plate.

2.4. Composite Property Testing

The mechanical properties of the composites of the grafted kenaf and the untreated kenaf were obtained by conducting the tensile tests, which were performed with Tensilon, Universal Testing Machine. The crosshead speed during the tension testing was 5 mm/min.

For water absorbency, the preweighted kenaf composites (both of the untreated kenaf and grafted-kenaf) were immersed in distilled water at room temperature for 24 hr. After immersion, the kenaf composites were dried in oven at 50°C , 24 hr and cooled in silica-gel contained dessicator prior to reweighted measurement. The different in weight before and after the test is expressed as the water absorbency performance.

III Result and Discussion

3.1. Confirmation of Grafting

The SEM images of untreated kenaf and the grafted kenaf fiber after 24 hours extracted by tetrahydrofuran are shown in Fig 1. Comparing both of those micrographs, it is obvious that the surface of fiber is thoroughly covered by polymer after graft treatment. This verify the incorporation of polymeric MMA have been incorporated with the kenaf fiber. The amount of grafted PMMA, however, could be reduced if only the improvement of the interface interaction between the fiber and matrix is required. The kenaf fiber with such grafted surface will have another possibility by itself as moldable composite material. Moreover, clarification by using FTIR analysis confirms the additional peak of carbonyl group at 1734 cm^{-1} . Those sharp peaks exhibit the ester group of PMMA on the grafted kenaf, and this also provides information that the process of grafting has been strongly occurred.

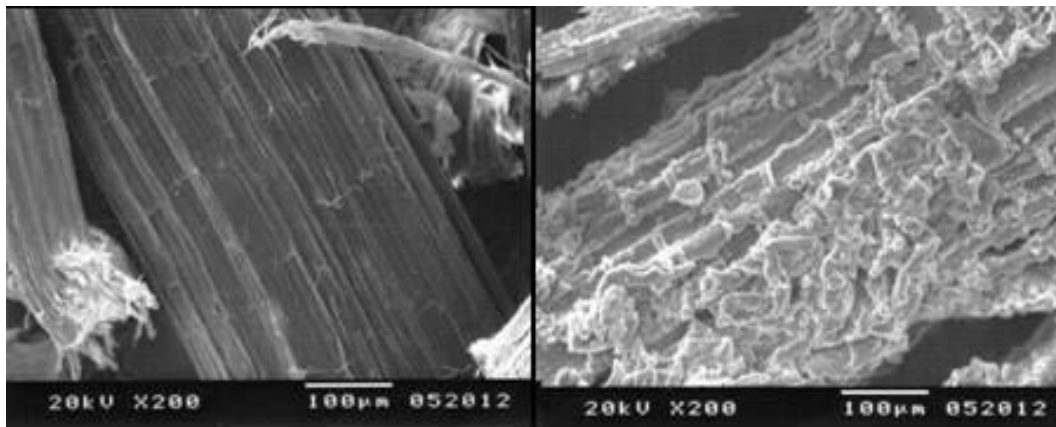


Fig. 1 SEM micrographs of (a) untreated and (b) MMA-grafted kenaf

3.2. Influence of Parameter Condition

3.2.1 Effect of Cerium Concentration

Fig. 2 shows the effect of ceric ion concentration on graft yield. It is evident that increasing of cerium concentration (from 10 to 50 mmol/L) results in the increasing of graft yield. The increase in the amount of initiator could lead to more formation of free radicals on kenaf to give the more reaction with MMA monomer and yield more grafting ratio as the consequence.

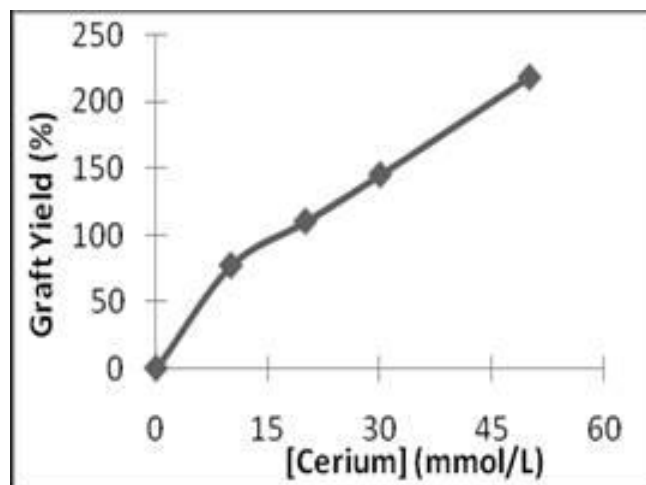


Fig. 2 Effect of ceric ion concentration on kenaf grafting yield.

3.2.2 Effect of Monomer Concentration

Fig. 3 represents the effect of monomer concentration on graft yield and graft efficiency. Graft yield was found to increase from 50 % to 201 % by increasing MMA monomer from 0.374 mol/L to 0.755 mol/L. Enhancement of graft yield can be associated with the fact that increasing monomer concentration would allow formation of grafting to grow and long graft chains were formed since the provided active sites are the same in all monomer concentration. However, increasing monomer concentration more than 0.75 mol/L make the graft yield to decrease. This is probably due to the precedence of homopolymerization, reducing accessibility of monomer to macroradicals at higher monomer concentration.

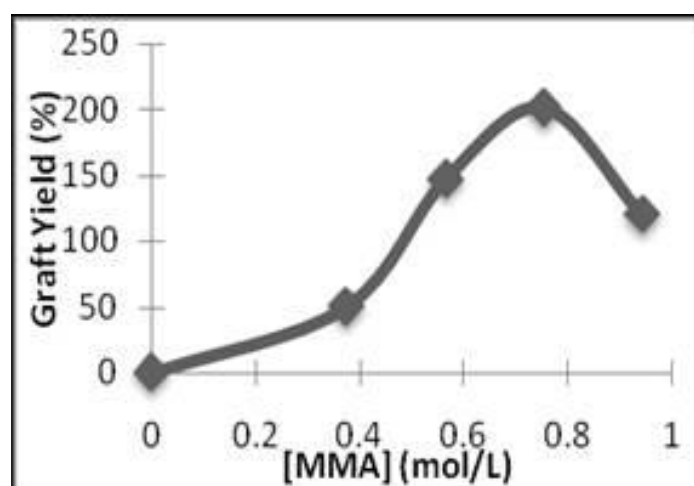


Fig. 3 Effect of monomer concentration on kenaf grafting yield.

3.2.3 Effect of Reaction Time

The influence of graft reaction time on graft yield is exhibited in Fig. 4 at the different graft temperature. From this figure, the graft yield is characterized to increase steadily with time until 3 h and then it tends to nearly level off with prolonged time reaction. The higher graft yield that occurred at higher temperature could be due to the more diffusion rate of monomer into the kenaf backbone which lead to the higher yields.

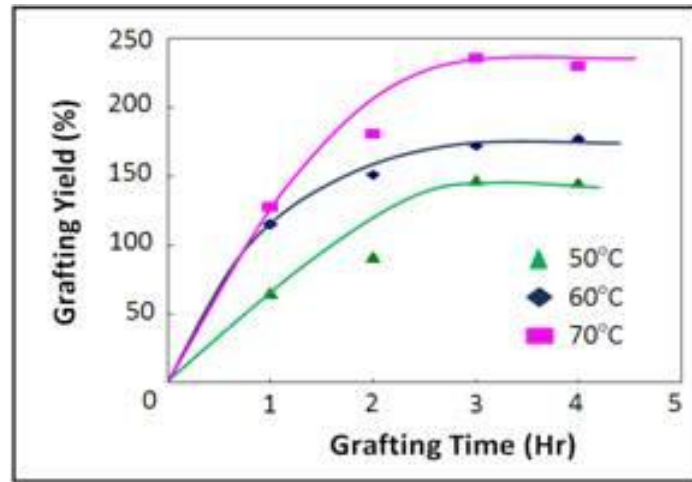


Fig. 4 Effect of graft reaction time on kenaf grafting yield.

Based on experiments above, the parameters of ceric ion concentration: 30 mmol/L; MMA concentration: 0.75 mol/L; reaction time: 3 hours have been chosen to prepare a large scale of PMMA-grafted kenaf fiber with graft yield about 160% for preparation of composite material.

3.3 PMMA-Kenaf Composite

3.3.1 Composite Properties

The photograph of the successfully molded hard plate is depicted in Fig. 5 for the untreated-kenaf and grafted-kenaf composites. The fibers are obviously appeared and combined with the transparent polymethyl methacrylate. The tensile strength of the composite sample is obtained from the stress-strain curve of the PMMA composites of the untreated kenaf, and the grafted-kenaf. Stress-Strain curve of the untreated and MMA-grafted kenaf composites is exhibited at Fig. 6. It can be shown that both of the curves are similar, except to their load values.

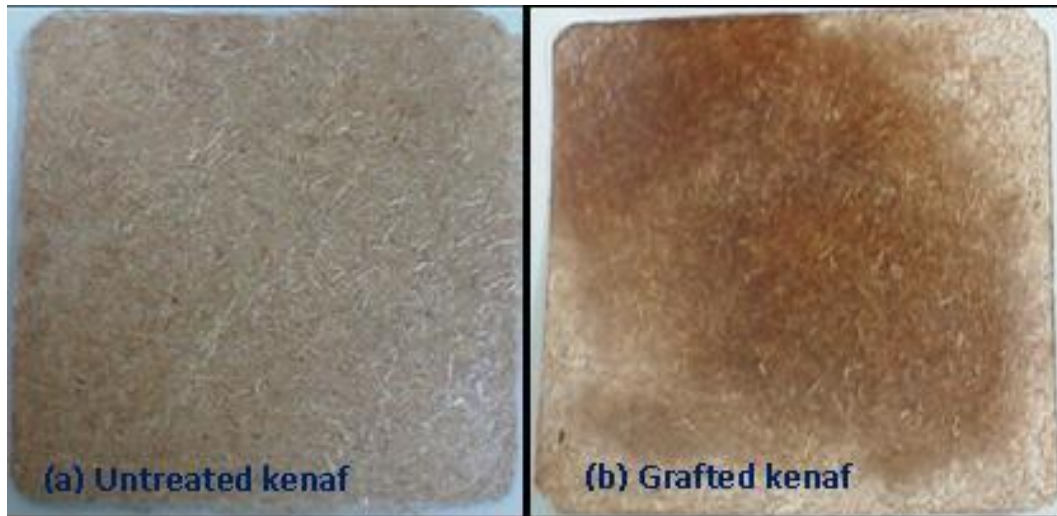


Fig. 5 Photograph of (a) untreated kenaf composite and (b) MMA-grafted kenaf composite.

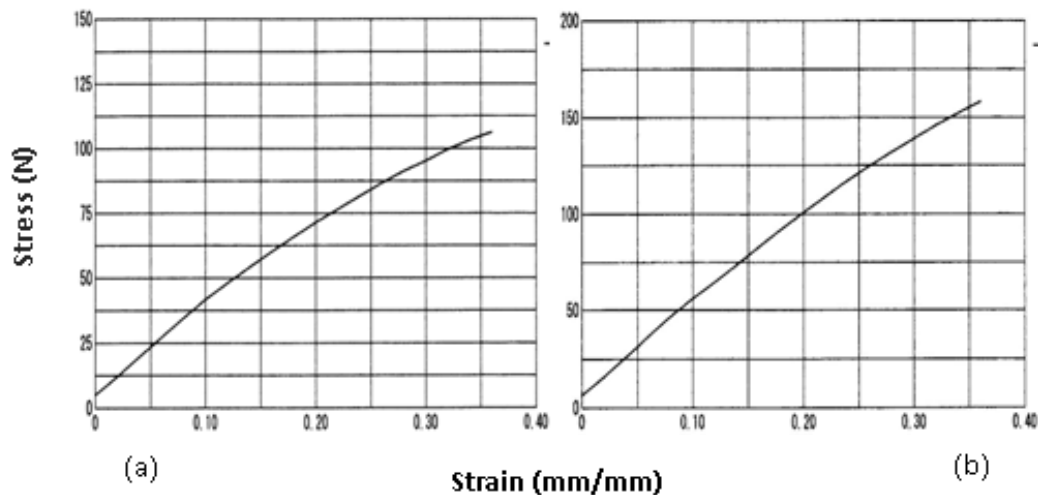


Fig. 6 Tensile strength result of (a) untreated kenaf composite and (b) grafted kenaf composite

There is a little change in slope around 0.1 strains, which may indicate the initial failure of the resin matrix. Continuing of tensile force beyond that point implies to the strength of the kenaf filler and resin matrix which depends on their interfacial adhesion, until composite breakage occurred at about 0.36 strain for both samples. Breakage of the untreated kenaf occurred at about 106 N, whereas, the grafted one happened at 163N.

From those figures, the tensile strength of untreated and the grafted kenaf composites were measure, and gave the value of 21.4 and 31.5 MPa, respectively.

From the significant increase value of the tensile strength, it could be said that the modification by graft polymerization method can improve the poor adhesion between PMMA matrix and kenaf fiber, which were shown by the impartment around 50% in tensile strength of the composites. This study also exhibits that the grafted polymer can function effectively as compatibilizer or interfacial agents to help forming a stronger combination between hydrophobic plastic material (methyl methacrylate) and hydrophilic natural kenaf fiber, evolving in development advanced composite materials.

The strong interaction between kenaf fiber and polymer matrix in the kenaf-polymer composite prepared by graft polymerization was confirmed from the analysis of the fracture surface of both of those composites. In case of the untreated kenaf composite, it is observed that kenaf fiber could not stop the crack propagation, therefore showing fiber have pulled-out experience from the matrix, leaving as many holes like depicted in Fig. 7 (a). This result indicates there is a poor interaction of fiber and polymer matrix. On the other hand, Fig. 7 (b) which represents the fracture surface of grafted-kenaf composite after tensile strength test, shows that there is no holes formed on the fracture surface of grafted-kenaf composite, since the compatibilized fibers may serve as sites for crack propagation to reduce energy required to break the specimen, leading to crack stopping at the fibers. From this result, it is notified that modifying of fiber surface by graft polymerization has improved the adhesion of kenaf fiber and polymer matrix.

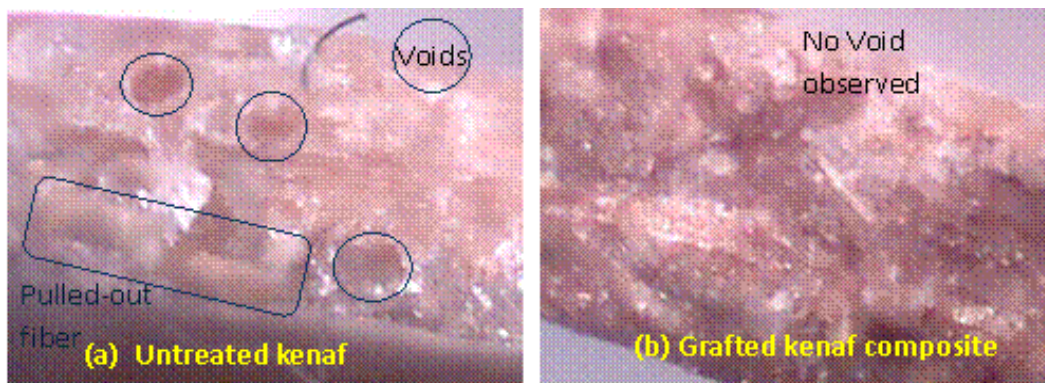


Fig. 7 The fracture surface of untreated kenaf composite and grafted kenaf composite after tensile strength test.

3.3.2 Water Absorbency

The water absorbency of lignocellulosic materials is generally considered from the interaction through hydrogen bonding of the hydroxyl groups on the containing cellulose with water molecules

Table 3.1 represents the results of water absorbency of kenaf-polymer composites after 24 h water immersion test. There is about 3.5 times improvement in reducing the water absorption of grafted-kenaf composite as compared to the untreated kenaf composite. Due to the behavior of fiber-polymer matrix of the latter composite, in

which has a poor adhesion than the former composite as previously explained, the cellulose microfibrils of the fibers can absorb as many water molecules into inside. However, graft polymerization of kenaf fiber by hydrophobic type of MMA monomer have changed the fiber surface to the water-repellent properties. This fact can lead a suggestion of the contribution of the grafted kenaf fiber that has less water absorption compared to the untreated kenaf fiber in a composite.

Table 3.1 Water absorbency of kenaf-polymer composites

Kenaf fiber used	Water absorbency (mg/mg)
Untreated kenaf	122
Grafted-kenaf	34

IV. Conclusion

The present study dealt on the development of lightweight composite material with the filler from renewable resource. Preparation of natural kenaf composites through hot pressing method were carried out after the kenaf filler had initially been modified by graft polymerization via cerium solution technique as the pretreatment method. It has been found that the cerium concentration and MMA monomer concentration and reaction time are significantly affecting the graft yield. The optimal grafting parameters (ceric ion concentration: 30 mmol/L; MMA concentration: 0.75 mol/L; reaction time: 3 hours) were then employed to facilitate a large amount of grafted kenaf (with graft yield ca. 160%) as a reinforcement material for preparing kenaf composite. In this study the composite has been produced with the fiber loading 40%. It has been found that there are more than 50% upgrading of tensile strength, as well as 3.5 times good improvement in water absorbency have been achieved as performance improvement of grafted kenaf composite towards the untreated one. The fiber gave its function to reinforce the composite strength and the clarified that PMMA-grafting process facilitates the surface compatibilizer to polymer matrix to improve the interfacial adhesion.

V. References

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