



ISSN:1991-8178

Australian Journal of Basic and Applied Sciences

Journal home page: www.ajbasweb.com



Surface Graft Polymerization of Methyl Methacrylate onto Plasma Activated Natural Kenaf Fiber

¹Tota Pirdo Kasih and ²Shin-ichi Kuroda

¹Department of Industrial Engineering, Bina Nusantara University, Jl. KH Syahdan No. 9, Palmerah, Jakarta Barat, Indonesia.

²Department of Production Science and Technology, Graduate School of Engineering, Gunma University, 29-1 Hon-cho, Oota, Gunma 373-0057, Japan

ARTICLE INFO

Article history:

Received 12 October 2014

Received in revised form 26 December 2014

Accepted 17 January 2015

Available online 28 February 2015

Keywords:

plasma-induced graft polymerization, natural kenaf fiber, methyl methacrylate

ABSTRACT

Hydrophobic poly(methyl methacrylate) (PMMA) has been grafted onto the surface of kenaf fiber via plasma-induced graft polymerization. The influence of irradiation time and RF plasma power were investigated in order to obtain the optimal parameters for maximum formation of peroxides. The peroxy groups were initially introduced to kenaf fiber through plasma treatment followed by oxidation in air and become the species that responsible to initiate the succeeding graft polymerization. It was found that the grafting did not yield any increase on fiber weight, therefore the grafted fiber was studied in more detail by performing characterization with XPS, SEM and TG/DTG. Through the SEM and XPS studies, it was confirmed that the surface topography and chemical composition of the grafted kenaf have been changed due to the presence of PMMA. TG/DTG measurement showed that the grafted polymer could improve the fiber vapor absorption and thermal stability, while keeping the fiber bulk properties similar to the untreated one.

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To Cite This Article: Tota Pirdo Kasih and Shin-ichi Kuroda, Surface Graft Polymerization of Methyl Methacrylate onto Plasma Activated Natural Kenaf Fiber. *Aust. J. Basic & Appl. Sci.*, 9(7): 269-272, 2015

INTRODUCTION

Plasma treatment and plasma polymerization have been generally recognized to be an attractive method for surface modification of polymers. Plasma, which consists of reactive species such as radicals, metastable molecules, charged particles of electrons and ions can make reactions through its species collisions with polymer surface to form variety of new species that are chemically active. These new species can interact with radical species in plasma leading to the formation of new functional groups, and also could initiate polymerization when contacted with monomer. Most of works regarding plasma-induced graft polymerization have so far dealt with surface modification of films or textile fibers (Gupta, 2001; Hocker, H., 2002) and rare research to modify the surface of plant fiber type materials.

Many efforts have been reported over the last few decades to the use of plant fiber in preparation of composite material, which is even recently still an active area of research (Yousif, 2012; Sui, 2009). Among the various plant fibers, kenaf (*hibiscus cannabinus L.*) is regarded as one of the most

expecting fiber due to its superior toughness and high aspect ratio in comparison with other fibers. Kenaf, a fast growing agro plant, predominantly composed of cellulose, lignin, hemicellulose and other constituents such as pentosan and ash. Kenaf has also been proven can absorb as much as 1.5 tons CO₂ per ton kenaf (Ofoegbu, 2012) which offering a source of the environmental friendly material.

The main drawback of kenaf is its hydrophilic nature due to three hydroxyl groups in the repeating unit of cellulose. Some reports have been made on the conventional graft polymerization onto plant fibers using chemical solutions (Khullar, 2008; Salam, 2005). However, those processes usually accompanied with damaging bulk fiber. Chemical disposal after treatment will moreover create another problem as the environmental pollution. Thus, in order to improve fiber surface characteristics with keeping its bulk properties, special treatment with the plasma-induced graft polymerization as the most likely, must be conducted to the surface of fiber. In the present study, low pressure glow discharge is studied to induce graft polymerization to modify fiber surface in placed of using chemical treatment.

Corresponding Author: Tota Pirdo Kasih, Department of Industrial Engineering, Bina Nusantara University, Jl. KH Syahdan No. 9, Palmerah, Jakarta Barat, Indonesia.
E-mail: tkasih@binus.edu

Experimental:**Plasma-induced Graft Polymerization:**

The kenaf fiber was produced in Anhui Province, China and supplied by Uni Corporation, Japan. The fiber was simply washed with boiling water and then dried in a vacuum dryer before used. MMA monomer was distilled under reduced pressure before used. Plasma-induced graft polymerization of MMA monomer onto kenaf fiber was carried out in two steps of process. First, the activation of kenaf surface by irradiation of air plasma. Kenaf fiber was put into the petri-dish and then placed on the sample holder at lower electrode in a bell-jar type plasma reactor. The system was evacuated until to the reduced pressure of 5 Pa. Flow gas controller was operated to introduce air into reactor and stabilize the pressure of 20 Pa before transmitting 13.56 MHz RF power supply through the electrodes. Plasma was generated at a different electric power and the fiber was exposed for a predetermined period of time. After the plasma treatment, the fiber was contacted with atmosphere for 5 min to form peroxides on the surface. Secondly, graft polymerization was carried out by placing fibers containing peroxy groups into the vessel and then immersed in 2 mL MMA monomer. After degassing thoroughly, the graft polymerization was thermally performed at 60°C for 5 h. In order to remove any adhered homopolymer, the grafted fibre was extracted with tetrahydrofuran (THF) over a night. The amount of peroxide formed on kenaf fiber after plasma treatment was determined according to the iodometric titration with the following procedure [8]: The plasma treated kenaf was placed in a flask containing solution of 20 mL

isopropyl alcohol, 5 mL saturated sodium iodide solution and 2 mL acetic acid. The mixed solution was refluxed at 85°C for 15 min, and then cooled to the ambient. The liberated iodine was titrated with 0.01 N standard sodium thiosulfate solution.

RESULTS AND DISCUSSIONS**Formation of Peroxides:**

It is known that oxygen containing functional groups can be introduced onto the surface of plasma treated polymers in the form of carboxyl, ketone, hydroxyl and peroxide (O'Hare, 2002) among which, peroxide is the most possible species that can initiate grafting in the presence of monomer. Table 1 summarizes the formation of peroxides on kenaf surface after the irradiation of air plasma.

It can be observed that increasing the plasma power as well as elongating the irradiation time did not result in more peroxides. The maximum amount of peroxide was obtained when the fiber was irradiated by plasma for 180 s at 5 W of plasma power. These parameters were therefore used for the process of thermal graft polymerization of MMA onto kenaf fiber.

Plasma-induced Graft Polymerized Sample:

It was found that the grafting did not yield any increase on fiber weight for the different plasma treatment time. Therefore, the presence of grafting was examined by using the following analysis tools due to the typical of plasma treatment that can modify material only on the surface area.

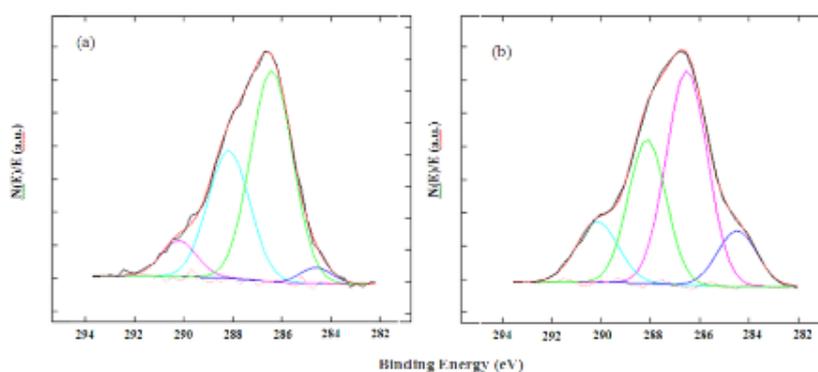


Fig. 1: High resolution of C1s core spectra of (a) untreated kenaf fiber and (b) plasma grafted kenaf fiber

X-ray Photoelectron Spectroscopy (XPS) Study:

XPS measurement was performed to investigate the changes in chemical atomic composition and to identify the chemical bonding existing on the fiber surface. Fig. 1 depicts the high resolution scans of the C1s core spectra with their deconvolution peaks for the untreated kenaf (1.a) and grafted kenaf (1.b). C1s core spectrum of kenaf fiber consists of four different peaks; at 284.5 eV for C-H/C-C, at 286.5 eV for C-

O, at 288.1 eV for C=O/O-C-O and at 290 eV for O-C=O. Characteristics of kenaf fiber surface are mostly indicated by C-O and C=O/O-C-O, among which C-O and O-C-O are the characteristic of for the pure cellulose (Pertile, 2010). However, rather high content at 288.1 eV peak and the lower percentage C-C and O-C=O components suggest that some hydrocarbon-rich compounds like lignin and some compounds such as fat or wax are present and

mixed well with cellulose. This is plausible since the raw kenaf was only extracted with hot water, which could not remove some compounds mentioned above.

The relative chemical bonds concentration from C1s core spectra deconvolution of both fibers are summarized in Table 2.

Table 1: Effect of irradiation time and power applied of air plasma on the formation of peroxides on treated kenaf fibers.

Sample	Irradiation time (s)	RF power (W)	Amount of peroxide (meq/100 g sample)
Untreated fiber	---	---	0
	60	5	0.69
	120	5	1.09
	180	5	1.49
	300	5	1.39
Treated fiber	180	2.5	0.49
	180	5	1.49
	180	10	1.29
	180	15	0.49

Table 2: Relative Chemical Components Concentration from Deconvolution of C1s Core Spectra of Untreated Kenaf Fiber and Grafted Kenaf Fiber.

Sample	C-H / C-C	C-O	C=O / O-C-O	O-C=O
Untreated kenaf	3.1	54.9	33.4	8.6
Grafted kenaf	11.6	46.6	28.7	13.2

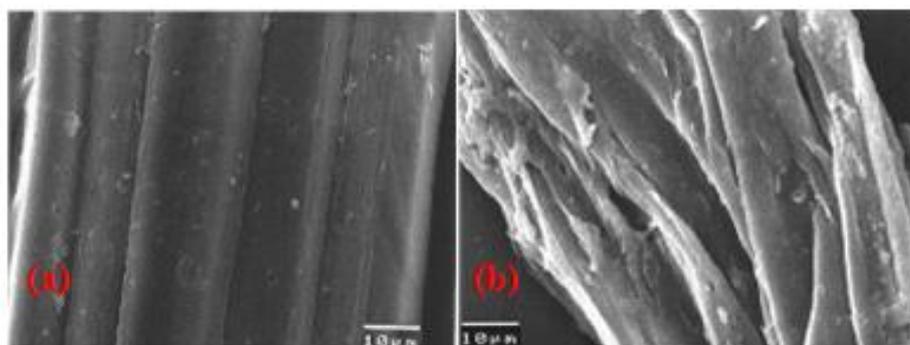


Fig. 2: SEM images of (a) untreated kenaf fiber and (b) MMA-grafted kenaf fiber.

Compared to the untreated fiber, an increase in C-C intensity to 11.6% and O-C=O concentration to 13.2% are attributed to the incorporation of methylene, methyl and ester groups of PMMA that are apparent for the grafted fiber. Accompanied to those increases are the decreases in C-O and C=O/O-C-O concentrations. These facts clearly confirm the grafting of PMMA on kenaf fiber.

SEM Micrograph:

Surface morphology of untreated and grafted fibers is shown in SEM images depicted in Fig. 2. The untreated fiber originally has a rather smooth surface topography. Several fibrils are bound together by middle lamella consisting mainly of lignin which still present on the surface. On the grafted kenaf, the PMMA masks can be seen covering the fiber in such a way which lead to the unsmoothed coverage of the fiber surface. The incomplete coverage could be due to the inhomogeneous activation of fiber surface due to only some surface area that having direct contact with the discharge and not activated on the underlying

region. Another reason is caused by the roughness surface that cause it variably susceptible to plasma treatment (Felix, 1994).

Thermal Behavior (TG/DTG):

Fig. 3 represents the TG and DTG curves of untreated and grafted kenaf and shows that process of thermal degradation could be divided into three steps. In the initial step, the first loss occurs on below 100°C which is attributed to the evaporation of absorbed water of the fibers. In the second step, initial thermal degradation that occurs around 300°C was represented by a shoulder in DTG curve. The last step relating to the major thermal degradation shows a maximum weight loss rate at 374°C. The curves of grafted fiber shows the decelerated weight loss below 100°C and the slightly shift to the right of the curve in total. The former should be the effect of PMMA layer on kenaf surface which make the fiber has low vapor permeability. On the other hand, the latter shows that the thermal stability of grafted kenaf fiber is higher than untreated kenaf fiber. This founding is interesting since the PMMA itself will be

decomposed completely around 375°C. This phenomenon can be explained that sort of cross linked chains were possibly occurred between the grafted polymer and kenaf molecule. The breakage of various linkages by plasma treatment could be compensated by this new type of crosslink formed

simultaneously with grafting, leading to the enhancement of thermal stability. Those curves are also clarify the bulk properties of the kenaf was sustained even after experinced the graft polymerization processes.

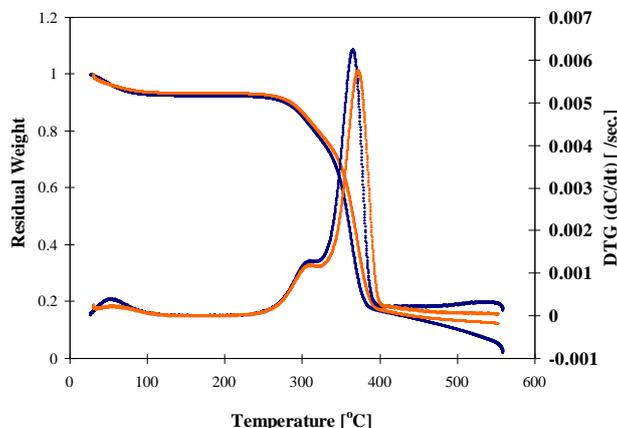


Fig. 3: TG/DTG curves of untreated kenaf fiber and grafted kenaf fiber.

Conclusions:

In this work, plasma-induced graft polymerization of MMA monomer onto kenaf fiber using air plasma was studied. Plasma discharge has been proved to assist the generation of peroxides after interaction with the air and it became the responsible active species to proceed the grafting in the presence of monomer. The amount of peroxides were apparently depended on the irradiation time and power applied. It was found that that there was no significant weight increase in grafted kenaf fiber after extraction with solvent. By carrying out the XPS, SEM and TG/DTG it was clarified that the graft polymerization of MMA onto kenaf only occurred on the partial fiber surface and let the bulk properties of the fiber keeps stable. This surface-modified kenaf fiber can be a good reinforcement for plastic matrix in preparation of more environment friendly composite material.

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