UNIVERSITI PUTRA MALAYSIA

RADIATION-INDUCED GRAFT COPOLYMERIZATION OF METHYL ACRYLATE AND ACRYLIC ACID ONTO RUBBER WOOD FIBER

SALIZA BINTI JAM

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By

SALIZA BINTI JAM

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia in Fulfilment of the Requirement for the Degree of Master of Science

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DEDICATION

To my beloved husband, Zul Hisham, whose patience, supports and companionship has facilitated my work. To “Mak” and “Abah”, and also my family thanks for everything.

Abstract of Thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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Chairman: **Dr. Mansor Hj. Ahmad**

Faculty: **Science and Environmental Studies**

Graft copolymerization of methyl acrylate and acrylic acid monomers onto rubber wood fiber (RWF) was carried out by simultaneous radiation-induced technique. The parameters affecting the grafting reaction were investigated and the optimum conditions for both monomers obtained are as follows: impregnation time, 16 hours; total dose, 30 kGy; methanol:water ratio, 3:1; monomers concentration, 40 v/v% and sulphuric acid concentration, 0.1 mol/L.

Fourier Transform Infrared (FTIR), Thermogravimetry Analysis (TGA), and Scanning Electron Microscope (SEM) analyses were performed to characterize graft copolymers. The structural investigation by X-ray diffraction (XRD) shows the degree of crystallinity of rubber wood fiber decreased with the incorporation of poly(methyl acrylate) and poly(acrylic acid) grafts which causes partial destruction of the inherent crystallinity in fiber. The sorption behavior of poly(acrylic acid)-grafted RWF resin toward some metal ions was investigated using a batch technique. The binding capacities of Cu, Fe, Zn, Cd and Pb ions were 0.379, 0.795,

0.189, 0.921 and 1.218 mmol/g, respectively. The sorption capacities of poly(acrylic acid)-grafted RWF resin were selectivity toward these metal ions is in the following order: Pb > Cd > Fe > Cu > Zn.

Irradiated PP/poly(methyl acrylate)-grafted RWF composite has higher mechanical properties than PP/poly(methyl acrylate)-grafted RWF composite because of EB-treatment of PP is a highly efficient technique of creating chemically active sites on PP matrix, which created a better coupling, and can be proved by SEM studies and TGA analysis. Generally, the addition of poly(methyl acrylate)-grafted RWF as coupling agent into the composites reduces the flexural and tensile properties, which, causes poor and incompatible dispersion, which leads to poor filler-matrix interfacial bonding. But, the addition of 1.0 wt % of P(MA)-*g*-RWF into the blend give an optimum value of flexural and tensile properties.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PENGKOPOLIMERAN CANGKUK TERARUH SINARAN METIL AKRILIK DAN ASID AKRILIT KE ATAS SERABUT KAYU GETAH

Oleh

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Pengkopolimeran cangkuk monomer metil akrilat dan asid akrilik ke atas serabut kayu getah telah dilakukan melalui teknik radiasi secara berterusan. Parameter-parameter yang memberi kesan terhadap pengkopolimeran telah dikaji dan keadaan optimum tindak balas yaang diperolehi untuk kedua-dua monomer adalah seperti berikut: masa rendaman, 16 jam; jumlah dos yang diserap, 30 kGy; nisbah metanol:air, 3:1; kepekatan momomer, 40 v/v%, dan kepekatan asid sulfurik, 0.1 mol/L.

Pencirian kopolimer cangkuk telah dilakukan melalui analisis spektroskopi inframerah, analisis termogravimetri dan fotomikrograf pengimbasan elektron mikroskop (SEM). Kajian struktur melalui pembelauan sinar-X (XRD) menunjukkan kandungan darjah penghabluran serabut kayu getah berkurangan dengan kemasukan poli(metil akrilat) dan poli(asid akrilik) di mana ia menyebabkan pemusnahan sebahagian hablur semulajadi serabut. Ciri serapan poli(asid akrilik) terhadap ion sebahagian logam telah dikaji melalui teknik

0.379, 0.795, 0.189, 0.921 dan 1.218 mmol/g. Kapasiti serapan resin kopolimer asid akrilit adalah mengikut susunan berikut: Pb > Cd > Fe > Cu > Zn.

Komposit PP tersinar/poli(metil akrilat)-cangkuk-serabut kayu getah mempunyai sifat mekanikal lebih baik daripada komposit PP/poli(metil akrilat)-cangkuk-serabut kayu getah kerana rawatan sinaran elektron (EB) ke atas PP merupakan teknik berkesan untuk mencipta tapak aktif di atas PP secara kimia, di mana ia menghasilkan campuran yang lebih baik dan ini dibuktikan melalui analisis-analisis SEM dan TGA. Secara amnya, penambahan poli(metil akrilat)-cangkuk-serabut kayu getah sebagai agen penggandingan ke dalam komposit merendahkan sifat mekanikal komposit tersebut, di mana ketidakserasian penyebaran berlaku yang menghasilkan ikatan antara permukaan pengisi-matrik yang lemah. Tetapi, penambahan berat 1.0 % poli(metil akrilat)-cangkuk-serabut kayu getah pada ke dalam adunan memberikan nilai optimum sifat mekanikal komposit tersebut.

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I am also greatly indebted to UPM and MINT for providing the analysis facilities and the Government for PASCA grant for me to complete the study successfully.

I certify that an Examination Committee met on 5th March 2002 to conduct the final examination of Graduate Student on her degree of Master of Science thesis entitled "Radiation-Induced Graft Copolymerization of Methyl Acrylate and Acrylic Acid onto Rubber Wood Fiber" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examonation Committee are as follows:

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This thesis submitted to the Senate of Universiti Putra Malaysia has been accepted as fulfilment of the requirement for the degree of Master of Science.

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that is has not been previously or concurrently submitted for any other degree at UPM or other institutions.

SALIZA BINTI JAM

Date: 28 MAR 2002

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LIST OF ABBREVITIONS

FTIR	Fourier-Transform Infrared
Irradiated PP/P(MA)-*g*-RWF	Irradiated polypropylene blends with poly(methyl acrylate)-grafted rubber wood fiber
Irradiated PP/ RWF	Irradiated polypropylene blends with rubber wood fiber
Irradiated PP/ RWF (treated 1% P(MA)-*g*-RWF)	Irradiated polypropylene blends with rubber wood fiber (treated with 1% poly(methyl acrylate)-grafted rubber wood fiber)
MINT	Malaysian Institute for Nuclear Technology Research
P(AA)	Poly(acrylic acid)
P(MA)	Poly(methyl acrylate)
P(AA)-*g*-RWF	Poly(acrylic acid)-grafted rubber wood fiber
P(MA)-*g*-RWF	Poly(methyl acrylate)-grafted rubber wood fiber
PP/RWF	Polypropylene blends with rubber wood fiber
PP/P(MA)-*g*-RWF	Polypropylene blends with poly(methyl acrylate)-grafted rubber wood fiber
RWF	Rubber wood fiber
SEM	Scanning Electron Microscope
TGA	Thermogravimetry Analysis
XRD	X-Ray Diffraction

CHAPTER 1

INTRODUCTION

Graft copolymerization onto fiber can be carried out by chemical and radiation method. Radiation method has been widely used to initiate grafting because it has many advantages over other conventional methods. In radiation processing, no catalyst or additives are required to initiate grafting. Generally in the radiation technique, absorption of energy by backbone polymer initiates a free radicals process. With chemical initiation, free radicals are brought forth by the decomposition of the initiator into fragments, which then attack the base polymer leading to radicals. Chemical initiation is however limited by the concentration and purity of initiators. However, in case of radiation processing, the dose rate of the radiation can be varied widely and thus the reaction can be better controlled.

Unlike the chemical initiation method, the radiation-induced process is also free from contamination. Chemical initiation often brings about problems arising from local overheating of the initiator. But in the radiation-induced process, the formation of free radicals sites on the polymer is not dependent on temperature but is only dependent on the absorption of the penetrating high-energy radiation by the polymer matrix. Therefore, radiation processing is temperature independent or, in other words, it is a zero activation energy process for initiation.

Significance of The Study

Since the event of worldwide ecological awareness, there has been a trend to produce low cost, biodegradable materials with improved properties. Lately, there has been a great interest to produce thermoplastic composites reinforced with natural products. In particular, cellulose fibers are becoming popular because they have lower cost and lower density and exhibit better processing flexibility and lower equipment wear than those of fiber glass, (Zadorecki and Mitchell, 1989; Raj and Kokta, 1991) which is still the common reinforcement. Also, cellulose fibers yield composites with better mechanical properties than those produced with materials such as wood floor and peanut shells (Maldas and Kokta, 1991; Raj *et al.*, 1990). However cellulose fibers have not been amply used because it is difficult to produce good dispersions of the fibers in the matrix due to the poor interfacial adhesion between them (Czarnecki and White, 1980). As the mechanical properties of composites depend on interfacial adhesion, it is necessary to have good adhesion between the reinforcement and polymeric matrix (Felix *et al.*, 1994).

To improve the interfacial adhesion between a polymeric matrix and cellulose fibers, a matrix-compatible polymer is commonly grafted to the fibers. Gaylord demonstrated that grafted cellulose, besides being more compatible with the matrix, helps to "compatibilize" nongrafted cellulose with the matrix (Gaylord, 1972). He also showed that composites with grafted cellulose have better processing properties and impact resistance than do those reinforced with nongrafted cellulose fibers

Graft copolymerization is a well-established technique for the modification of the physical and chemical characteristics of polymers. The nature of modification, for example, improvement in textile performances, depends on the properties of monomer. The properties of the grafted copolymer depend not only on the type of the monomer but also on the grafting level and distribution of monomer units. For example, the grafting of PMMA onto wool fabric improved textile performances such as dyeing, moisture regain and mechanical properties (Bashar *et al.*, 1995; Varma and Sadhir, 1978). However, further increase in graft yield was found to cause a slight reduction in moisture regain (EL-Naggar *et al.*, 1996).

In the past, extensive research has been carried out on radiation-induced grafting of acrylic acid, acrylamide, methyl methacrylate (MMA), styrene, and acrylonitrile onto polyethylene, poly(vinyl chloride), and nylon (Chapiro, 1958; Stannett, 1990; Trivedi *et* al., 1975). Very limited works (Garnett and Ng, 1996; Khan and Ahmad, 1997; Zahran and Zohdy, 1986) have so far reported on the effectiveness of radiation-induced grafting onto cellulosic fiber. Therefore, this research has been carried out to fulfill the requirements.

Rubber wood is a widely used material due to its many excellent properties such as its aesthetic appearance, lightness, strength, ease of workability and wide availability. Nevertheless, it has some limitations. Rubber wood is cellulosic-based fiber and a hygroscopic material that swells when it absorbs water and conversely, shrinks when it is dried. It is susceptible to insect and fungal attack and undergoes decay especially in environments like those in the tropics. In order to improve water resistant, cellulose is already widely modified by acetylation with acetic anhydride (Youngquist *et al.*, 1986). The modification of cellulose through grafting with monomers was investigated in order to produce hydrophilic/hydrophobic fiber.

In this work, the surface modification of rubber wood fiber by radiation-induced grafting methyl acrylate (MA) and acrylic acid (AA) in methanol-water system by using γ-irradiation from Co^{60} source as a mean of initiation was examined. Graft copolymerization was carried out by mutual or simultaneous method in air. Percentage of grafting was determined as functions of total dose, methanol composition in reaction solution, concentration of monomer, and concentration of sulphuric acid (H_2SO_4). FTIR, TGA and XRD were used to characterize the grafted fiber.

Objectives of The Study

The objectives of this study are as follows:

1. To graft methyl acrylate and acrylic acid onto rubber wood fiber using simultaneous graft copolymerization technique.
2. To study the effecting reaction parameters to obtain an optimum condition of grafting.
3. To characterize rubber wood fiber-grafted methyl acrylate and acrylic acid by Fourier Transform Infrared Spectroscopy, thermogravimetry, X-ray diffraction, and scanning electron microscopy.

4. To prepare bio-composite materials from rubber wood fiber-grafted methyl acrylate and to characterize the mechanical properties of the blends.
5. To prepare ion exchange materials from rubber wood fiber-grafted acrylic acid and to study metal ion and carboxylic acid capacity using atomic absorption spectrophotometer.

CHAPTER II

LITERATURE REVIEW

Rubber Wood

Rubber wood is the Standard Malaysian Name for the timber of *Hevea brasiliensis*. This species has been planted in Peninsular Malaysia for the past hundred years mainly for its latex. Though there is only one species of rubber tree planted in Malaysia, there are numerous clones are developed to achieve a higher yield of latex, and little has been done to improve the tree from on volumetric yield of wood from these trees.

Rubber wood trees are normally replanted after attaining the age of 25 - 30 years where they are generally attain a clear bole of more than 10 meters tall (Westgarth and Buttery, 1965). Diameter of these trees could easily reach 500 mm at breast height. However, trees of newer clones are usually shorter and smaller. Boles of the seedling trees are usually strong tapered.

General Characteristics

Rubber wood is light timber with air-dry density ranging between 560 – 650 kg/m^3 averaging 640 kg/m^3 (40 lb/cu. ft.). The sapwood is generally not distinguishable from the heartwood. The wood is whitish yellow or pale cream when freshly cut, and seasons to a light straw or light brown in color with a slight pinkish tinge. The wood texture ranges from moderately coarse to coarse, with grain ranging from straight to shallowly interlocking.

Durability

Although rubber wood in its natural from is classified as non-durable and found to be susceptible to attack by fungi and insects, the durability can be enhanced easily by proper treatment methods.

Mechanical Properties

Standard mechanical test, similar to the methods outlined in B.S. 373:1957 for 50 mm specimens and A.S.T.M. D143-52 have been conducted on rubber wood and the results are presented in Table 1, together with similar strength properties of other popular Malaysian timbers, to facilitate ease of comparison. The basic and grade stress of this timber have been worked out based on the formulae by Chik (1980a), and are presented in Table 2. The timber falls in Strength Group C following the criteria for strength grouping of Malaysian timbers (Chik, 1980b).

Results from steam bending trials indicated that rubber wood bends better than Kapur (*Dryobalanops aromatica*) and some of the White Merantis (*Shreaa spp.*). Rubber wood bends are very stable after they are left to set (Ser and Lim, 1980).