

Synthesis and characterization of *Dioscorea hispida* sp. tuber starch-polyacrylamide wood coating and its facile inhibitory towards *Pycnoporus sanguineus* and *Coptotermes curvignathus*

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ABSTRACT

A unique, non-leaching and durable novel anti-biocide polyacrylamide-starch coating (pAam-g-S) has successfully been synthesized. In this study, a grafted cationic-functionalized polymeric coating was designed and cross-linked with native starch extracted from *Dioscorea hispida* sp. yam to afford multi-functional anti-fungal and anti-termite coating. Leaching of the disinfectant into the environment was eliminated because no toxic chemicals were used. The copolymerization was successfully carried out to produce various ratios of pAam-g-S coating using modification of starch-gel. Results obtained from Fourier Transform Infrared-Attenuated Total Reflectance (FTIR-ATR) confirmed the monomer pAam was grafted onto the starch backbone as shown by the cross-linked peak at 1642 cm^{-1} . Supported by differential scanning calorimetry (DSC), the highest transition glass temperature was observed at $154\text{ }^{\circ}\text{C}$. The coating was designed to continuously decontaminate against pathogenic fungus and termite in addition to afford preliminary anti-biocides properties. Facile anti-fungal and anti-termite evaluations were conducted via total weight loss of wood (%) studies using white rot fungus, *Pycnoporus sanguineus* and termite *Coptotermes curvignathus* respectively. In order to verify the coating performance, gel fractions, morphologies and heat resistant properties were also investigated.

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1. Introduction

Wood is a natural polymeric composite which is widely used for home furnishings and construction materials. Although this organic multifunctioning material offers many applications, however unprotected wood is susceptible to wood rotting fungi and termite, which resulted in quality curtailment particular in its mechanical strength [1]. In order to extend the service life, wood products are therefore normally treated with preservatives such as creosote, alkaline copper quaternary (ACQ), and copper azole (CuAz) [2,3]. These chemicals were used as protector due to their impregnation ability into the wood cell and furthermore improve their physical durability. A range of different chemicals are readily available to improve the permanence as well as to help the resis-

tance to decay, insects, weather or fire. Some of the preservative agents are highly toxic that will be phased out in a short period of time as it is largely imposed adverse impact on human health and polluted the environment. Therefore, the quest for alternative phytochemicals with lower environmental and mammalian toxicity has currently become a major concern.

The search for biocides with improved antimicrobial and functional performance has led to the development of several generations of cationic quaternary ammonium salts (QAS) which were widely used to control the bacterial growth in clinical, industrial and marine environments [4]. Quaternary ammonium salts have been used as key components in many disinfectants, fabric softeners, laundry detergents, and antistatic agents [5,6]. QAS has high biocide activity for a wide spectrum of biological species at minimal concentrations and can be easily tailored for desired functionality and alkyl chain length through conventional synthesis method [5–7]. Although the synthetic bioactive such QAS is often demonstrated as a good disinfectants, on the contrary, it is poor

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in degradability which consequent lead to pollution. Alternately, coating with high presence of copper (Cu) [8–10] contents which leached out relatively in high amounts could be toxic in aquatic environments [10,11].

Utilizing essential oil extracted from herbs or plants to suppress mold on surfaces to inhibit the attack of the decay fungi, and to protect against termites on wood has proved to be a powerful alternative. Anti-fungal effects of essential oils extracted from lemongrass, rosemary, tea tree, thyme, cinnamon, anise oil, lime oil, and tangerine oil have been reported for mold growth on wood but on contrary of their good performance it is difficult to extract essential oils as it requires lots of procedures and time consuming, whereas it is not practical to produce the disinfection agent. So far there were no reports on anti-fungal effects on wood by *Dioscorea hispida* sp. yam starch, or their alkaloid (dioscorin) components. However from the previous research [12], it was reported *Dioscorea Hispida* sp. starch gave positive inhibition of several bacterias such as *Staphylococcus Aureus* sp., *Staphylococcus Aureus* sp., *Sacharomyces Cereviae* sp. and *E. Coli* sp.

Owing to this matter, durability and effectiveness become the main focus as self-decontaminating coatings with eco-friendly property is developed. Therefore, natural materials such as starch, cellulose and chitosan have attracted great attention due to their abundant resources, degradability and ease of manipulation. It is noted that natural based material can be decomposed and be used by microbes, plants as well as being compatible to the environment. Hence, alternative has been made by using organic resources which offers greener application without any side effect [13].

Starch tubers are abundant bio-resources which comprises 40–60% of natural amylose and amylopectin. Nonetheless, starch from different wild tubers species are unutilized due to poisonous bioactive alkaloids that are harmful to human [13]. *Dioscorea hispida* sp. or locally known as Ubi Gadong in Malaysia, a poisonous tuber that stores its toxic poison in its rhizome. Approximately there are over 600 *Dioscorea* species found in various parts of the world, especially in tropical and subtropical region [14,15]. *Dioscorea hispida* Dennst. (Dioscoreaceae), another wild tuber despite its toxicity has become a staple food in some tropical regions. Traditionally it has also been used as one of the medicinal remedies to treat constipation. Studies have shown that an alkaloid extract from these tuber causes dizziness, nausea, vomiting, and caused sleepiness in humans [16,17]. Starch from the tuber of *Dioscorea hispida* is edible and can be consumed when the poison (dioscorine) has been removed. It takes five to seven days of soaking in which to ensure full detoxification in flowing water [18–20]. Furthermore, it has been used as remedy in which the tuber was used as crude drug to inflammation [21].

Previously we demonstrated that hydrogel made from *Dioscorea hispida* sp. starch can act as a promising antibacterial to inhibit bacterial activity [12,22–24]. Hence in this research, the chemical and physical characteristics of the *D.hispida* starch based coatings with its anti-fungal and anti-termite were further explored. One-pot reaction method has been used in preparing the coating by grafting starch with polyacrylamide (pAam) was employed [24]. The characterization was made by using Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM), Optical microscopy, and Differential Scanning Calorimetry (DSC). Polyacrylamide are known to have excellent impact strength, low curing temperature, and abrasion resistant characteristics [25]. The promising applications for biocide containing this polyacrylamide include foams, coatings and medical devices [26,27]. This research embraced the characterization of this coating to determine its optimum performance including its facile anti-fungal and anti-termite test. The coating was treated on the rubberwood and followed by

Feeding Inhibitory test (FI test) as specified in ASTM D2017- (ASTM 1996).

2. Experimental

2.1. Materials

Analytical grade chemicals were used in this studies. All solutions without any further purification were prepared using distilled water. The *dioscorea hispida* sp yam was obtained from Terengganu, Malaysia. The polyacrylamide (Sigma Aldrich) was used without further purification. As for the cross-linking agent and initiator, *N,N'*-methylenebisacrylamide (MBA) (Merck 8) and potassium persulfate (KPS) (Merck) were used. A Denver 215 model pH meter and a Heidolph MR3001 model magnetic stirrer were also used during the experiments. Retsch PM200 model grinder was used to grind the starch compound into fine powder with diameter of approximately (5 nm). A polyscience 9006 model refrigerating-heating circulator was also used during the starch based hydrogels synthesis. This refrigerating-heating circulator was used to ensure that all chemical process such as radicals and crosslinking polymerization were performed without any effects from the surrounding physically and chemically.

2.2. Preparation of starch and starch stock solution

Past research stated *Dioscorea hispida* (*D.hispida*) tuber has been recognized as a poisonous plant in which its tuber contains toxic poison and can be only consumed after the poison is properly removed [28]. The wild yam tubers were peeled and rinsed before being pulverized using a home blender. The suspension was kept in a container and left overnight. After 24hr, the upper layer of the suspension was removed while the lower layer was collected and dried in the oven for 3 days. The dried starch was then pulverized until 1??m diameter using ultron grinder.

2.3. Synthesis of *dioscorea hispida* sp starch/polyacrylamide coating

About 2 g of *D. hispida* sp. starch was mixed in 10 mL (5 w/v) of sodium hydroxide solution with constant stirring at 300 rpm at ambient room temperature to form gelatinized starch mixtures for 1 h. Later, gelatinized starch mixtures were added with 0.25 g MBA and initiator. The flask was stoppered well and the contents were stirred and refluxed with monomer polyacrylamide at constant temperature of 60 °C at 400 rpm. In order to establish crosslinking, an inert condition has to be applied by flowing nitrogen into the reflux. This condition was adhered to avoid the formation of bubbles in the casted coating and also to enhance crosslinking between the monomer and starch. The mixtures were then into molded petri dishes and dried at room temperature. The coating obtained were 50% translucent and labelled with various ratios of monomer and starch.

2.4. Characterization of the hydrogels

FTIR-ATR analysis was conducted to characterize the coating films using Perkin-Elmer Spectrum BX-II Model FTIR spectrophotometer. Samples were dried to a constant weight in an oven at 50 °C for 24 h before being used and certain peaks of the samples were recorded in the range between 4000 cm⁻¹ and 400 cm⁻¹, at a resolution of 4 cm⁻¹ as an average of 50 scans.

The surface of the samples were observed with a JEOL JS-6300F Scanning Electron Microscope (SEM) operated at an acceleration voltage of 5 kV. In addition, further surface analysis were done by using optical scanning digital microscope. The samples

were pinned on a mounting board and surface topography was analyzed with an enhanced 1.3 megapixels (20×–220× resolution) AM4515ZT Optical Scanning Microscope operated with the adjustable polarization.

Rubberwood was used as the test sample in this study. The mass and dimensions of the wood block specimens (16 × 16 × 10 mm³ cubes) accurately determined. The wood blocks were placed in beaker, covered with a coarse mesh, and weighed down. Subsequently, polymeric polymer particle suspension (New Preservative) with various the concentration (0, 1, 3, 5 & 10%) w/v of PVOH and starch extract will be poured over the block. The beaker was subjected to a pressure treatment consisting of a partial vacuum of 17.3 kPa for 25 min, followed by pressurization at 790 kPa for 45 min. Specimens were first removed and the excess liquid was wiped off. The wood blocks were then weighed to determine the mass of the retained suspension, and the undelivered polymeric particles were recovered consecutively. This is due to further confirm the delivered mass of polymeric particles. The samples were dried overnight (40 °C), cut longitudinally into four wafers (two interior and two exterior), and reweighed. The wafers then will be sterilized in an autoclave for 15 min at 120 °C.

2.5. Resistance of particle boards to fungal decay

The decay resistance against the white rot fungus, *P. sanguineus*, was carried out in the laboratory using the method specified in ASTM D2017-81 (ASTM 1996). The efficacy of the treatment was assessed based on the per cent of weight loss caused by fungal degradation. Eight test blocks, 16 × 16 × 10 mm, were cut from each treated and untreated boards. The blocks were stabilized in an air-conditioning room with temperature maintained at 25 ± 2 °C and 65 ± 5% relative humidity until they reached constant weight. The test bottles were prepared according to ASTM D2017-81 (ASTM 1996). Rubberwood feeder strips of dimensions 3 × 20 × 30 mm were laid flat on the soil surface in the test bottles. The bottles were loosely capped steamed and sterilized at 121 °C for 30 mins. After cooling and keeping overnight, the feeder strip in each bottle was later inoculated with the white rot fungus. The fungus was allowed to grow and cover the feeder strip before the pre-weighed test block was introduced. The bottles together with the contents were left in an incubating room with temperature maintain at 25 ± 2 °C and (70 ± 5)% relative humidity. At the end of 12 weeks, the test blocks were removed from the bottles and all mycelium adhered on the surface of the blocks were brushed off. They were again left in the conditioning room until their weights were constant. The percent weight loss was represented in equation 1 where W_a were calculated from the conditioned weight before and W_b after exposure was obtained.

$$\frac{W_a - W_b}{W_a} \times 100 \quad (1)$$

2.6. Resistance of particleboards to termite attack

The test on resistance of treated boards against termite (*C. curvignathus*) was carried out in the laboratory in accordance with ASTM D3345-74 (ASTM 1998). Eight blocks of 25 × 25 × 10 mm were randomly cut from each of the untreated and treated boards and conditioned in the air-conditioning room until they reached constant weights. The weights were measured and the blocks were placed in test bottles filled with sand. The test bottles and the sand were prepared according to ASTM D3345-74 (ASTM 1998). The bottles, together with their contents, were sterilized at 120 °C for two hours. Approximately 1.0 ± 0.05 g termites comprising 10% soldiers and 90% workers were introduced in each of the test bottles. The bottles were covered with black paper and kept at room temperature 26 ± 1 °C for four weeks. The activities of the termites were

observed and the mortality recorded at the end of 1st, 2nd and 4th week of exposure. At the end of four weeks, the blocks were removed, cleaned and conditioned in a conditioning room until their weights were constant. The resistance to termite attack was calculated based on percentage weight loss from the conditioned weight before W_1 and after exposure W_2 . The percentage mortality of termites presented in equation 2 as calculated based on the number of dead (N_o) and the original number (N_i).

$$\frac{N_o}{N_i} \times 100 \quad (2)$$

3. Results and discussion

3.1. Synthesis of polyacrylamide and *Dioscorea hispida* sp. starch (pAam-g-S) coating

A proposed mechanism for synthesis of pAam-g-s (polyacrylamide-g-starch) coating, where acrylic radical polymerization with starch is a chain reaction process as shown in Fig. 1 consists of three main steps: initiation, propagation and termination [27,28]. Firstly, hydroxyl free radicals are formed on the starch backbone, a process initiated by KPS. Then, the pAam monomer reacts with the hydroxyl free radicals resulting in propagating a new polymer chain (branch) that is covalently anchored to the starch. The free radical site is then transferred to the newly formed branch. Subsequently, more pAam monomers may covalently bind to the free radical sites of the branch [29–31]. The propagation of the branch continues until termination occurs either by crosslinking of two growing starch chains with MBA or by a disproportionation mechanism [32]. Propagation and termination may also occur by a chain transfer to monomer, initiator, dead polymer, or to impurities. This shows that starch plays a major role in the synthesis of S-g-pAam coating. Firstly, it provides high density hydroxyl groups. Secondly, starch serves as the backbone of the coating networks, which determines the mechanical properties and machinability of the produced material.

3.2. Fourier transformed infrared (FTIR)

FT-IR spectra of the S-g-pAam coating and the starch are shown in Fig. 2. As can be seen, the S-g-pAam hydrogel and starch showed an absorption peak at 3274 cm⁻¹ and 3198 cm⁻¹ respectively due to the hydrogen bonded –OH groups of starch. Both reported peaks around 2931–2928 cm⁻¹ that referred to the –CH₂– asymmetric stretching of –CH₂OH groups in starch. For S-g-pAam coating, a broad peak appeared in the range of 1655.06 cm⁻¹, which assigned to the C=O stretching vibration of CNH₂C=O groups of grafted pAam with starch. Sharp peaks were observed at 1424 cm⁻¹ and 1415 cm⁻¹ in both pAam and S-g-pAam spectra which contributed from the carboxylate symmetric stretching of COO⁻ groups [33]. The peaks observed at 1655–1651 cm⁻¹ and 1415 cm⁻¹ prove the existence of carbonyl groups in coating after grafting polymerization. In comparison with the original starch, the FT-IR spectrum of S-g-pAam coating exhibits the absorption at 1077 cm⁻¹ for the C–O stretching while the vibration of –CH₂OH groups decreased due to the conjugation compared to the peak at 1077 cm⁻¹ (starch) [34]. This result was considered as previous researcher postulated that grafting polymerization reaction only occurred at the primary hydroxyl groups of starch. However, the existence of carboxyl groups is also possible due to the blending of pAam monomer or its homopolymer. As a consequence exhaustive washing procedure was conducted by immersing the coating in a 0.01 mol/L of NaOH for two days followed by freeze dry. The treated coating displays similar FT-IR absorption with the untreated sample, which further

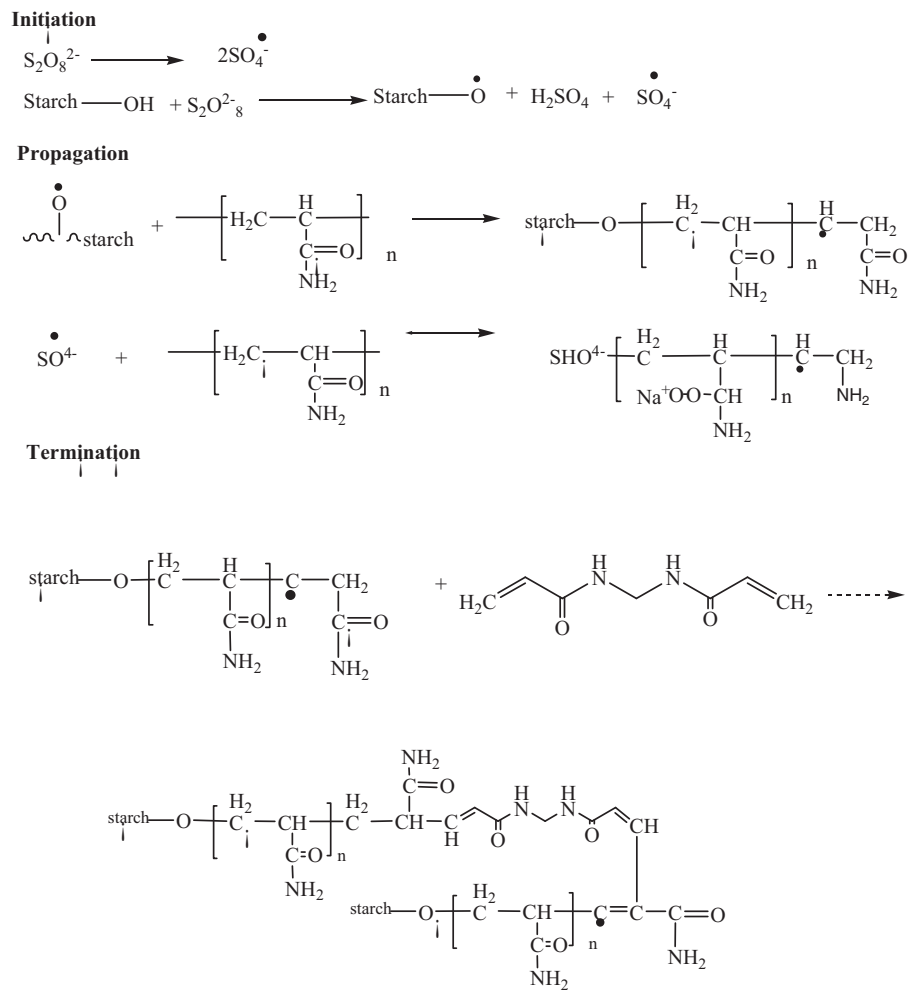


Fig. 1. Proposed mechanism for synthesis of polyacrylamide grafted dioscorea hispida sp starch enhanced with potassium persulfate (KPS) as the initiator and methylenebisacrylamide (MBA) as the crosslinked agent.

confirmed that pAam was successfully grafted to starch instead of blending with starch.

3.3. Scanning electron microscopy

Typical SEM photographic image in Fig. 3 shows that the coating are translucent, soft, and smooth with a slippery surface. From the previous study [35] suggests that the hydrogels had a highly porous network structure. As a higher mole ratio of polyacrylamide to starch was used, the strength of the final product is so poor that the coating can hardly be shaped. The SEM images in Fig. 3 showed non porous network structure with a maximum of 10 μm has been produced. Surface morphology of different ratios of starch/acrylamide complexes showed that the amount of starch used directly affected the surface topography of the coating ratios (3b, 3c and 3d). As can be seen, the coating with a ratio of 2:1 gave the most translucent and homogeneous surface compared to the coating gel with a higher amount of starch (Fig. 3c and d).

3.4. Optical scanning microscope

The images produced by Optical Scanning Microscopy in Fig. 4 displayed non-porous network topography on the surface of the starch based coating film with a maximum magnification of 200 μm . It also confirmed the resultant coating was uniform and homogeneous, with slightly porous surface with an average rough-

ness of 155.3 μm (Fig. 4). Surface morphology of different ratio of starch/polyacrylamide complexes showed that the amount starch used directly affected the smoothness of the grafted coating complexes 4a, 4b and 4c. Fig. 4a showed the ratios of grafted coating pAam-g-s 2:1 while Fig. 4b and c showed the ratios of grafted coating pAam-g-s 1:2 and 3:5 respectively. From the figures topography, it significantly displays a homogeneous surface with very limited porosity. The porosity of the coating has been successfully controlled by the incorporation of Tween-80 surfactant with the synthesized coating pAam-g-s. The process was likely to prevent the pores from absorbing too much water and hindered oxidation from occurred on the surface of the coated material. It has been reported [36] that the basic pH of the monomer aids in producing micro porous aggregates that can enhance the mechanical properties of the synthesized coating. Another important aspect during synthesis of coating between starch and pAam is that the mixture should not have any phase separation in order to obtain a maximum homogeneity. Film coating with a ratio of 2:1 gave the most homogeneous and smooth morphology compared to the other two coating ratios with a higher amount of starch as shown in Fig. 4.

3.5. Differential scanning calorimetry (DSC)

The differential scanning calorimetry analysis (DSC) component gave thermograms of starch and S-g-pAam coatings at different ratios a (starch), b (2:1), c (1:2), and d (3:5) as shown in Fig. 5. It was

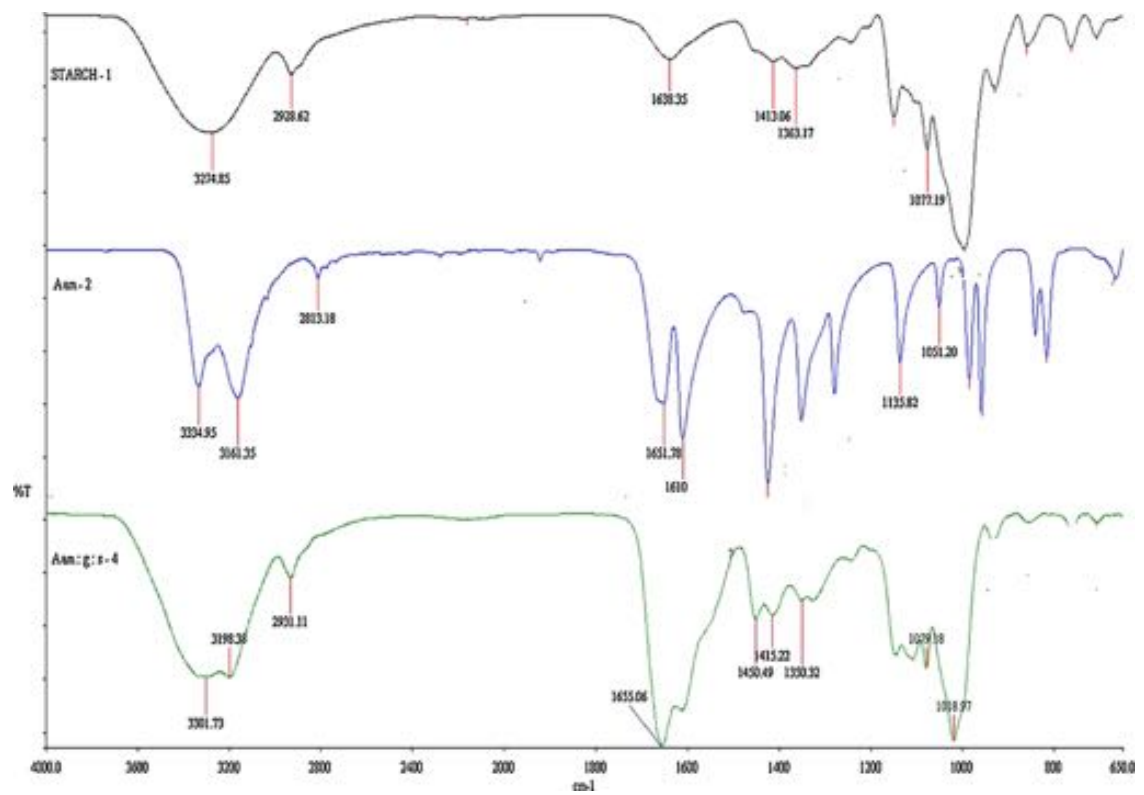


Fig. 2. FTIR spectra of monomer (pAam), cross-linked agent (MBA), Starch (comonomer), and grafted coating film (S-g-pAam).

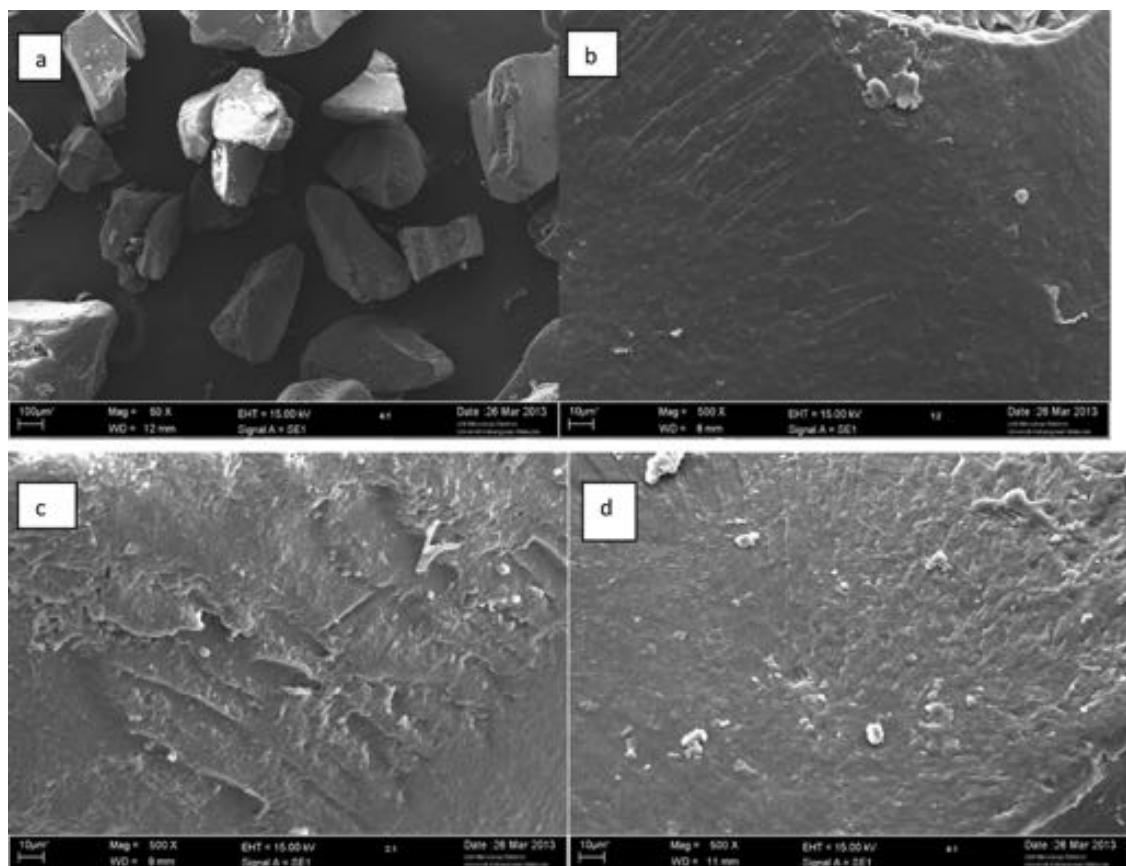


Fig. 3. Micrographs of a) *Dioscorea hispida* sp. starch granules b) polyacrylamide: starch (2:1) c) polyacrylamide: starch (1:2) and d) polyacrylamide: starch (3:5).

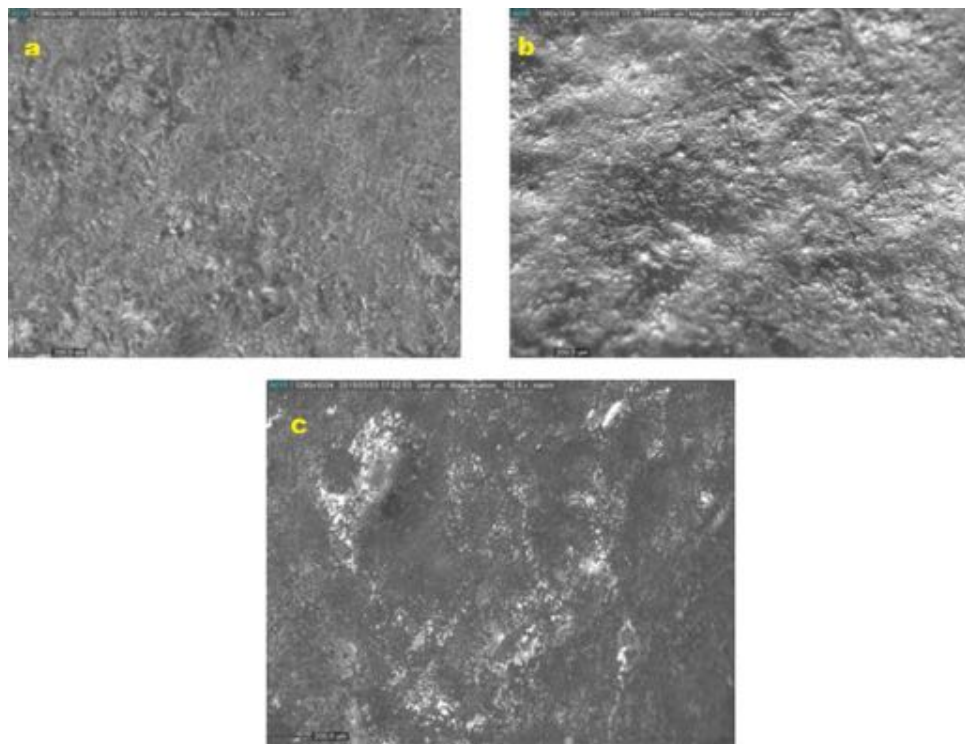


Fig. 4. Micrographs upon 150 times magnification (200 μm) of three pAam: starch ratios (a) 2:1 (b) 3:5 (c) 1:2.

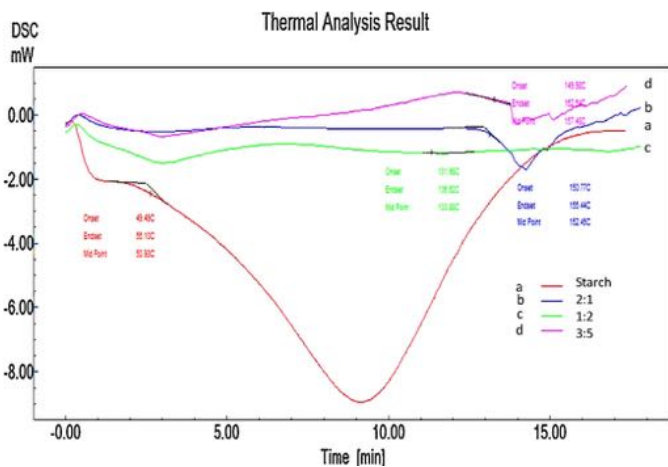


Fig. 5. Thermograms of different ratios of the coating sample: (a) starch powder only, coating ratio of pAam: starch (b) 2:1, (c) 1:2, (d) 3:5.

noted the differences in starch and monomer ratios significantly influenced the glass transition temperature (T_g) of the coatings. These results indicated many multistep taking places including the dehydration of carbohydrate chains and the breaking of C—O—C glycosidic bonding of the starch chain occur in the range 0°C – 60°C . However, there are prominent differences on the transitional glass temperature between the grafted pAam and starch. It has higher transitional glass temperature range compared to the original starch (T_g) which is 18.08°C whereas the grafted coating samples for ratio 1:2, 2:1 and 3:5 (T_g) in the range of 138.88°C , 152.45°C and 157.48°C respectively. It is concluded that the grafted coating film (S-g-pAam) were thermally stable which coincided with the amount of starch existed in the networks. On the other hand, the starch not only strengthens the networks but also acts as heat barrier which further enhances the thermal stability of the coatings.

3.6. Coating effect towards white rot fungus *Pycnoporus sanguineus* and termite *Coptotermes curvignathus*

3.6.1. Effect towards white rot fungus *Pycnoporus sanguineus*

White rot fungi is the sole microorganisms that efficiently degrade all the components of plant cell walls, both carbohydrates and lignin. As such species, e.g., *Pycnoporus sanguineus*, *Ceriporiopsis subvermispora* and *Trametes versicolor* have been studied in detail and used as model organisms for this complex process. These species could lead to severe damages to wood used for export and consequently affect the economical side. Apart from that, *C. curvignathus* termite also has been affected in the agricultural, silvicultural and horticultural sectors. In past research they reported that in agriculture, it is a serious pest of rubberwood (*Hevea brasiliensis*) grown on peat soils in Indonesia and Thailand. These fungi have been threatening the rubber tree by attacking trunks and as well the roots. Although on land that has been long planted or replanted with rubber, where the incidence of pest attack appears to be higher [37].

The inhibitory effects of grafted starch coating and their components on molds and the white-rot decay fungus *P. sanguineus* and termite *C. curvignathus* are shown in Fig. 6a and c. It is evident that the grafted coating S-g-pAam, exhibited both fungistatic and fungicidal activities against the test molds. *Dioscorea hispida* starch proved to be a stronger inhibitor to the test molds at various concentration. The synthesized starch based coating was coated on wood samples by dipping method to investigate its inhibition ability on the growth of the decay fungus, *P. sanguineus*. The samples tested shown in Fig. 6b and c was varied with three different ratios of polyacrylamide and starch which is 1:2, 2:1 and 3:5 to observe its preliminary inhibition towards fungus *P. sanguineus* and invasion of termite *C. curvignathus* respectively. From Fig. 6(iii), it can be concluded that the ratio starch up to 5g, gave the most effective inhibitory characteristic. The inhibition effect could be related to the existence of dioscorine-type alkaloids in the tubers which gave remarkable disinfection effects [12,38]. The results a



Fig. 6. (a) Rubberwood before coated with pAam-g-S coating while (b) Coated rubberwood affected by white rot fungi *P Sanguineus* with various ratios pAam: starch i) 2:1, ii) 1:2, and iii) 3:5. (c) Coated rubberwood attacked by termites *C. Curvignathus* while (d) Various ratios of coated rubberwood affected by *C. Curvignathus* with pAam: starch i) 2:1, ii) 1:2, and iii) 3:5.

Table 1

Mean weight loss of untreated and treated rubberwood after 12 weeks of exposure to *P. sanguineus*.

	Weight loss (%) ± SD				
	Concentration of dioscorea hispida grafted polyacrylamide preservative (w/v)				
Rubberwood	0 (control)	01:01	01:03	01:05	01:10
	33.25 ± 7.33	15.45 ± 4.53	5.43 ± 0.98	5.99 ± 0.68	5.17 ± 0.65

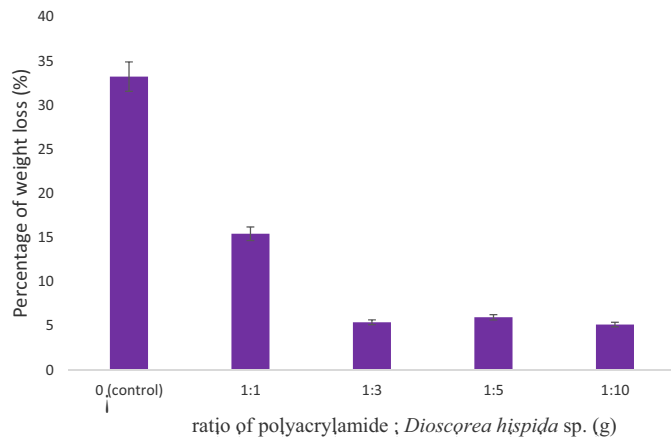
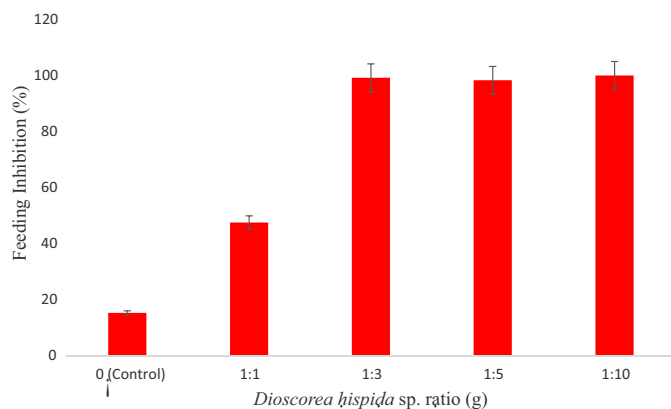
in agreement with previous research, where they demonstrated the hydrogels made with additional of *D hispida* sp. starch gave highly resistant to some bacteria and fungi [12,39,40] The presence of a cyclic chain in the disc-type molecule with nitrogen bonding with the carbon group (C–N) gives antioxidant ability, including anti-biocide properties against certain fungal and bacterial species (Table 1) [41,42].

From the preliminary result shown in Fig. 6, the anti-fungal and anti-termite were further investigated by conducted the total weight lost (%) and feeding inhibitory (FI) test. The purpose of the investigation was to study the effect of starch content towards the inhibition potential over *P Sanguineus* and *C. Curvignathus*. For optimum result, starch content of the coating ratio were increasing

from 1 g up to 10 g whereby polyacrylamide was remained constant with 1 g. Fig. 7 shows the observation of the total weight loss towards white rot fungi *P. sanguineus*. Found that the control (0%) of rubberwood which has not been coated, gave the highest weight loss (%) with 33.25 ± 7.33, attacked by *P. sanguineus*. However, convincing result was obtained for sample with concentration ratios of 1:1 (pAam-starch) where it able to reduce up to 15.45 ± 4.53 for the total weight lost (%) of rubberwood. The concentration ratios of 1:3 (pAam: starch) provided the optimum inhibition of the fungus. Result showed a moderate amount is required 3% of the starch ratio provided the best protection against *P. sanguineus*. Some of the pestiferous alkaloids that naturally exist in plant can inhibit the growth, cause morphological and physiological changes and affect

Table 2Effect of wood extracts on feeding inhibition (FI) and lethal concentration (LC50) on *C. curvignathus*.

	Ratio of <i>D. hispida</i> sp. grafted polyacrylamide preservative (w/v)				
	0 (Control)	1:1	1:3	1:5	1:10
Feeding Inhibition (%) ± SD	15.32	47.56	99.21	98.32	100.0

**Fig. 7.** Graph total percentage weight loss (%) of rubberwood treated with various ratio of *dioscorea hispida* sp. starch towards white rot fungi *P Sanguineus*.**Fig. 8.** Feeding Inhibition (%) of rubberwood towards termite *C. Curvignathus* as a function of *Dioscorea hispida* sp. ratio (g).

the reproduction of basidiomycetes. Fungal species and strains differ in their sensitivity toward certain chemical molecule such as nitrogen N in the protection mechanisms involved. Although heavy metals such as Hg, Cu, or Ni were relentlessly used in development of antifungal wood preservatives, however the utilization of these toxic inorganic metals consequently harmful to human and environment due to their leaching out from the sample [43].

3.6.2. Effect of wood extracts on feeding inhibition (FI) and lethal concentration (LC50) on *C. curvignathus*.

Termites serve a great role in recycling plant and woody materials, as they decompose the cellulose and help to break down approximately one third of the annual production of dead wood. Unfortunately, they are also highly destructive insect due to their wood eating habits. They destroy structural and non-structural building materials, finished goods, plants and agricultural crops and also other domestic goods such as paper, cloth, carpets and other cellulosic materials [42,44]. Hence this section discusses the effectiveness of *Dioscorea hispida* sp. wood coating as a function of *C. curvignathus* (Table 2).

Fig. 8 displayed effect of wood extracts on feeding inhibition (FI) and lethal concentration (LC50) on *C. curvignathus*. Control (0) was attacked by *C. curvignathus* shows 15.32% feeding inhibition. As the ratio of concentration increase to 1:1 (pAam-g-starch) the increment of (%) ± SD feeding inhibition is evident at 47.56%. In comparison for ratio 1:3 and 1:4 the percentage for feeding inhibition is vigorously increased up to 99.21 and 98.32%, respectively. As shown in tabulated data, the ratio 1:3 concentration of pAam-g-starch gave optimum feeding inhibitory by termites *C. curvignathus*. It is expected that by increasing starch to 10 equivalent ratio total feeding inhibitory upon termites are obtained. These results are clearly supporting previously discussed in section (i).

Contemporary protection methods include both physical and chemical approaches. Physical methods include physical barriers such as stainless steel mesh or gravel aggregates, heat, freezing, and microwaves have been used to control the termite invasion [45]. For example, Termimesh™ a commercial stainless steel mesh is not commonly employed as one of the termite barriers. Chemical barriers include the use of chemical termiticides in the soil around the structure to be protected. On the other hand, chemical treatment of wood is a common and effective method which is widely used to prevent termite damage. Although this approach is found workable however, some of the chemicals used are toxic and problematic occurs when this poisonous compound leach out or mishandled. In order to alleviate these concerns, it is necessary to look for alternatives to minimize the use of synthetic and harmful chemicals. Bio-pesticides, which are extracted or purified substances from plants potentially promising replacements due to advantages such as their minimal toxicity, widespread availability and relatively low cost.

4. Conclusion

Starch grafted polyacrylamide (S-g-pAam) coating was synthesized using *N,N'*-methylenebisacrylamide as a cross-linking agent and its potential inhibition was examined. There were absorptions in the FTIR spectrum of the coatings that significantly differ from the peaks corresponding to their individual components. Thus, it shows that the functional groups in the structure of starch and polyacrylamide change significantly. The cross-linking peak of starch and polyacrylamide was expected at the frequency absorptions 1655 cm^{-1} of Fourier Transformation Infrared. Topography of the surfaces of the synthesized S-g-pAam coating were determined via Scanning Electron Microscope (SEM) in the $10\text{ }\mu\text{m}$ magnification and Optical Scanning until 220 x micron resolution. It shows a homogeneous, smooth and translucent morphology that applicable for coating system. Differential Scanning Calorimetry (DSC) shows a convincing results towards thermal degradation of grafted coating pAam-g-S. Coating with ratio pAam: S 3:5 shows the highest transition glass temperature observed at $157\text{ }^\circ\text{C}$. Further investigation is made, to determine the effectiveness of native starch *Dioscorea Hispida* sp extract upon total weight loss (%) of rubberwood towards white rot fungi *P Sanguineus* and feeding inhibition (FI) of *C. curvignathus*. Results showed disinfection test of termites infectants (white rot fungus *Pycnoporus sanguineus* and termite *curvignathus*) occurred at an optimum sample ratio which was 1:3 pAam:starch. This formulation gave total inhibitory to both of the infectants. Based on the result obtained, S-g-pAam coating has the potential to be used as novel organic preservatives and biopreservatives.

cides which gave major decontaminating factor for prolonged the structure of rubberwoods.

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References

- [1] T.B. Yen, H.T. Chang, C.C. Hsieh, S.T. Chang, Antifungal properties of ethanolic extract and its active compounds from *Calocedrus macrolepis* var: *formosana* (Florin) heartwood, *Bioresour. Technol.* 99 (2008) 4871–4877.
- [2] S.S. Cheng, J.Y. Liu, E.H. Chang, S.T. Chang, Antifungal activity of cinnamaldehyde and eugenol congeners against wood-rot fungi, *Bioresour. Technol.* 99 (2008) 5145–5149.
- [3] F.L. Hsu, P.S. Chen, H.T. Chang, S.T. Chang, Effects of alkyl chain length of gallates on their antifungal property and potency as an environmentally-benign preservative against wood decay fungi, *Int. Biodeterior. Biodegrad.* 63 (2009) 543–547.
- [4] A.J. McBain, R.G. Ledder, L.E. Moore, C.E. Catrenich, P. Gilbert, *Appl. Environ. Microbiol.* 70 (2004) 3449–3456.
- [5] J. Hazziza-Laskar, G. Helary, G. Sauvet, Biocidal polymers active by contact. IV. Polyurethanes based on polysiloxanes with pendant primary alcohols and quaternary ammonium groups, *J. Appl. Polym. Sci.* 58 (1) (1995) 77–84.
- [6] R.R. Pant, P.A. Fulmer, M.B. Harney, J.P. Buckley, J.H. Wynne, Synthesis and bioadhesive efficacy of self-spreading polydimethylsiloxane oligomers possessing oxyethylene-functionalized quaternary ammoniums, *J. Appl. Polym. Sci.* 113 (4) (2009) 2397–2403.
- [7] R.R. Pant, B.T. Rasley, J.P. Buckley, C.T. Lloyd, R.F. Cozzens, P.G. Santangelo, J.H. Wynne, Synthesis, mobility study and antimicrobial evaluation of novel self-spreading ionic silicone oligomers, *J. Appl. Polym. Sci.* 104 (5) (2007) 2954–2964.
- [8] J. Balsiger, J. Bahdon, A. Whiteman, The utilization, processing and demand for rubberwood as a source of wood supply, *Forestry Policy and Planning Division*, 2000.
- [9] L. Waldron, P. Cooper, T. Ung, Prediction of long-term leaching potential of preservative-treated wood by diffusion modeling, *Holzforschung* 59 (5) (2005) 581–588.
- [10] A. Temiz, U.C. Yildiz, T. Nilsson, Comparison of copper emission rates from wood treated with different preservatives to the environment, *Build. Environ.* 41 (7) (2006) 910–914.
- [11] K. Stook, T. Tolaymat, M. Ward, B. Dubey, T. Townsend, H. Solo-Gabriele, G. Bitton, Relative Leaching and aquatic toxicity of pressure-treated wood products using batch leaching tests, *Environ. Sci. Technol.* 39 (1) (2005) 155–163.
- [12] I. Azman, S.A. Mutalib, S.F.M. Yusoff, S. Fazry, A. Noordin, M. Kumaran, A.M. Lazim, Novel *Dioscorea hispida* starch-based hydrogels and their beneficial use as disinfectants, *J. Bioact. Compat. Polym.: Biomed. Appl.* 31 (1) (2016) 42–59.
- [13] P. Hron, J.S. Lechtová, K. Smetana, B. Dvořáková, P. Lopour, Silicone rubber-hydrogel composites as polymeric biomaterials IX. Composites containing powdery polyacrylamide hydrogel, *Biomaterials* 18 (1069) (1997).
- [14] T. Agbor- Egbe, S. Treche, Evaluation of chemical composition of Cameroonian yam germplasm, *J. Food Compos. Anal.* 8 (1995) 274.
- [15] Salam A. Abdullah, *Poisonous Plants of Malaysia*, 1st ed., Tropical Press Sdn. Bhd, Kuala Lumpur, 1990 (pp. 19).
- [16] E. Leete, A.R. Pinder, Biosynthesis of dioscorine, *Phytochemistry* 11 (11) (1972) 3219–3224.
- [17] E. Leete, R.H. Michelson, Biosynthesis of dioscorine from trigonelline in *Dioscorea hispida*, *Phytochemistry* 27 (12) (1988) 3793–3798.
- [18] S.K. Hahn, *Yams: Dioscorea spp. (Dioscoreaceae)*, in: J. Smartt, N.W. Simmonds (Eds.), *Evolution of Crop Plants*, Longman Scientific and technical, UK, 1995, pp. 112–120.
- [19] M. Nashriyah, Y. Nornasuh, T. Salmah, N. Norhayati, M. Rohaizad, *Dioscorea hispida* dennst. (Dioscoreaceae): an overview, *Buletin UniSA* 4 (2010) (2180-0235).
- [20] J. Tattiyakul, T. Naksriarporn, X-ray diffraction pattern and functional properties of *Dioscorea hispida* dennst. starch hydrothermally modified at different tem-peratures, *J. Food Bioprocess Technol.* (2010), <http://dx.doi.org/10.1007/s11947-010-0424> (Online first).
- [21] M.H.H. Razali, H.H. Muhammad, N.A. Mohd, W.I.W. Ismail, A review on farm mechanization and analysis aspect for *Dioscorea hispida*, *J. Crop Sci.* 2 (1) (2011) 21.

- [22] Regina Sonthanasamy, A. Sisika, et al., Transformation of crystalline starch nanoparticles into highly luminescent carbon nanodots: toxicity studies and their applications, *Carbohydr. Polym.* 137 (2016) 488–496.
- [23] A. Ashri, M.S.M. Yusof, M.S. Jamil, A. Abdullah, S.F.M. Yusoff, M.N.M. Arip, A.M. Lazim, Physicochemical characterization of starch extracted from Malaysian wild yam (*Dioscorea hispida* Dennst.), *Emir. J. Food Agric.* 26 (8) (2014) 652.
- [24] A.A. Prabu, M. Alagar, Thermal and morphological properties of silicone-polyurethane-epoxy intercrosslinked matrix materials, *J. Macromol. Sci. Part A—Pure Appl. Chem.* 42 (2) (2005) 175–188.
- [25] Q.Y. Tong, G.W. Zhang, Rapid synthesis of a superabsorbent from a saponified starch and acrylonitrile/AMPS graft copolymers, *Carbohydr. Polym.* 62 (2005) 77–84.
- [26] R.M. Hudzari, M.A.H.A. Ssomad, Y.M. Rizuwan, M.N.N. Asimi, A.B. Abdullah, Development of automatic alkaloid removal system for *Dioscorea hispida*, *Front. Sci.* 1 (1) (2011) 16–20.
- [27] J.P. Zhang, A. Li, A.Q. Wang, Study on superabsorbent composite. VI. Preparation: characterization and swelling behaviors of starch phosphate-graft-acrylamide/attapulgite superabsorbent composite, *Carbohydr. Polym.* 65 (2006) 150–158.
- [28] G. Moad, D.H. Solomon, *The Chemistry of Radical Polymerization*, 2nd ed., Elsevier Ltd, Oxford, 2006.
- [29] A. Hebeish, J.T. Guthrie, *The Chemistry and Technology of Cellulosic Copolymers*, Springer-Verlag, Berlin, 1981.
- [30] D. Roy, M. Semsarilar, J.T. Guthrie, S. Perrier, Cellulose modification by polymer grafting: a review, *Chem. Soc. Rev.* 38 (7) (2009) 2046–2064.
- [31] G.M. Kavanagh, S.B. Ross-Murphy, Rheological characterisation of polymer gels, *Prog. Polym. Sci.* 23 (3) (1998) 533–562.
- [32] E. Karadağ, B. Ö. Üzümlü, D. Saraydin, Swelling equilibria and dye adsorption studies of chemically crosslinked superabsorbent acrylamide/maleic acid hydrogels, *Eur. Polym. J.* 38 (11) (2002) 2133–2141.
- [33] M. Ayyanar, S. Ignacimuthu, Ethnomedicinal plants used by the tribals of Tirunelveli hills to treat poisonous bites and skin diseases, *Indian J. Tradit. Knowl.* 4 (2005) 229–236.
- [34] J. Tattiyakul, T. Naksriarporn, X-ray diffraction pattern and functional properties of *Dioscorea hispida* dennst starch hydrothermally modified at different temperatures, *J. Food Bioprocess Technol.* (2010), <http://dx.doi.org/10.1007/s11947-010-0424-3> (Online first).
- [35] Y. Zhou, S. Fu, H. Liu, S. Yang, H. Zhan, Removal of methylene blue dyes from wastewater using cellulose-based superadsorbent hydrogels, *Polym. Eng. Sci.* 51 (12) (2011) 2417–2424.
- [36] J.X. Wang, L.X. Wen, Z.H. Wang, J.F. Chen, Immobilization of silver on hollow silica nanospheres and nanotubes and their antibacterial effects, *Mater. Chem. Phys.* 96 (2006) 90–97.
- [37] J.P. Zhang, A. Li, A.Q. Wang, Study on superabsorbent composite. VI. Preparation: characterization and swelling behaviors of starch phosphate-graft-acrylamide/attapulgite superabsorbent composite, *Carbohydr. Polym.* 65 (2006) 150–158.
- [38] M. Verma, S. Sharma, R. Prasad, Biological alternatives for termite control: a review, *Int. Biodeterior. Biodegrad.* 63 (2009) 1–14.
- [39] A. Ashri, A. Lazim, A study on the effect of the concentration of *N,N*-methylenebisacrylamide and acrylic acid toward the properties of *Dioscorea hispida*-starch-based hydrogel, *The 2014 UKM FST Postgraduate colloquium: Proceedings of the Universiti Kebangsaan Malaysia, Faculty of Science and Technology 2014 Postgraduate Colloquium Vol. 1614* (September (1)) (2014) 251–255 (AIP Publishing).
- [40] S. Shanthakumari, V.R. Mohan, A.J. De Britto, Nutritional evaluation and elimination of toxic principles in wild yam (*Dioscorea spp.*), *Trop. Subtrop. Agroecosyst.* 8 (2008) 313–319.
- [41] P. Baldrian, Interactions of heavy metals with white-rot fungi, *Enzyme Microb. Technol.* 32 (1) (2003) 78–91.
- [42] A. Zaidon, et al., Efficacy of pyrethroid and boron preservatives in protecting particleboards against fungus and termite, *J. Trop. For. Sci.* (2008) 57–65.
- [43] R.K. Upadhyay, G. Jaiswal, S. Ahmad, L. Khanna, S.C. Jain, Antitermite activities of *C. decida* extracts and pure compounds against Indian white termite *Odontotermes obesus* (Isoptera: odontotermitidae), *Psyche* (Stuttg) 20 (2012) 1–9.
- [44] S.M. Seo, J. Kim, S.G. Lee, C.H. Shin, S.C. Shin, I.K. Park, Fumigant antitermitic activity of plant essential oils and components from Ajowan (*Trachyspermum ammi*), Allspice (*Pimenta dioica*), caraway (*Carum carvi*), dill (*Anethum grave-olens*), Geranium (*Pelargonium graveolens*), and Litsea (*Litsea cubeba*) oils against Japanese termite (*Reticulitermes speratus* Kolbe), *J. Agric. Food Chem.* 57 (15) (2009) 6596–6602.
- [45] A. Gupta, S. Sharma, S.N. Naik, Biopesticidal value of selected essential oils against pathogenic fungus, termites, and nematodes, *Int. Biodeterior. Biodegrad.* 65 (5) (2011) 703–707.