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Surface Behavior and Film Formation Analysis of Sisal Fiber Coated by Polymethylmethacrylate Ultrathin Film

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Abstract

Admicellar polymerization was applied to modify the sisal fiber surface with polymethylmethacrylate in order to improve the compatibility between sisal fiber and surrounding polymeric matrix in composite. The effect of the amount of monomer (methyl methacrylate) and initiator (sodium persulfate) on the hydrophobicity behavior and PMMA film formation of the admicellar-treated sisal surface was studied. The increase in the hydrophobicity of the admicellar-treated sisal fiber was examined by the flotation test, moisture absorption, and electrostatic charge or zeta (ζ) potential. The amount of PMMA film formed on sisal surface was investigated by the weight loss of the admicellar-treated sisal extracted by acetone and chloroform, and thermal degradation by thermogravimetric analyses. The admicellar-treated sisal can float on water surface for longer than half an hour and its moisture absorption decreased. The ζ potential of its surface also shows a significant change compared to the untreated sisal. The results from the weight loss indicated that the amount of PMMA formed on the sisal fiber surface depended upon the amount of monomer and initiator. The Fourier transform infrared spectrum of the admicellar-treated sisal shows the characteristic peaks of PMMA and the scanning electron microscopy micrograph of the treated sisal was obviously different from the untreated sisal confirming that there was a thin film coated on the admicellar-treated sisal fiber.

Keywords: sisal fiber, admicellar polymerization, film formation, surface characterization

1. INTRODUCTION

Sisal fiber accounts for almost half of the total production of commercially used natural fibers. In addition, sisal fibers, which are extracted from the leaves of the sisal plant (*Agave sisalana Perr*), are widely grown in tropical zone including Thailand. At present, sisal fiber is mainly used as ropes, twines, cords, upholstery, padding and mat making, fishing nets, fancy articles *etc*. During the past decade, the use of sisal fiber as an economical and environmental friendly reinforcement for polymeric composites has raised great interest. However, sisal, which is a cellulose fiber, typically has poor interfacial adhesion with hydrophobic polymer matrix and low moisture resistance leading to a decrease in the durability of the composites. Recent developments in the chemical and thermal methods for the modifications of sisal fiber surface in order to enhance the adhesion between sisal fiber and surrounding polymeric matrix and to reduce water absorption were reviewed by Li and *et al* [1]. The chemical composition and mechanical properties of sisal fiber are summarized in Table 1 [2]. Currently, there are several new methods for improving the natural fiber-polymer compatibility, for example, alkaline treatment [3,4], silane treatment [4,5], and graft copolymerization of monomer directly on the surface [5,6,7]. The surface treatment by admicellar polymerization is one of the new surface modification methods proposed as the competitive method for compatibility enhancement in composite. Admicellar polymerization process is generally carried out in an aqueous system of surfactant solution in order to form the admicelle on subtract surface as a two dimensional container for polymer-film former organic monomer.

In general, cellulose fibers contain a large number of hydroxyl groups in their chemical structure as shown in Figure 1a and in aqueous system the polar groups with negative charge occur through interactions with water molecules as illustrated in Figure 1b [8]. The charge of sisal surface can be investigated by measuring its ζ potential in aqueous solution at different pH. In order to control the surface charge and/or the hydrophobic/hydrophilic character of the surface, surfactants which are adsorbed at the solid-liquid interface can be used. The adsorption of a cationic surfactant causes a decrease in the negative ζ potential down to zero, which is the iso-electric point. In order to form the admicelle of surfactant on cellulose fiber, cationic surfactant can be used. However, pH and counter ion can increase the amount of surfactant adsorbed on the fiber surface to form the admicelle needed for the admicellar polymerization process.

Admicellar polymerization is an innovative method, first investigated by Wu and *et al* [9]. It can be used to improve the compatibility at the interface between different materials. In previous work admicellar polymerization has been used to improve the adhesion in polymeric composites such as, precipitated silica with polystyrene [10] and copolymer of styrene-butadiene and styrene-isoprene [11], glass fibers with polystyrene [12] and copolymer of isoprene-styrene [13]. There are also many researchers applying admicellar polymerization technique to other areas for various purposes by coating different polymers on different materials [9, 14-19]. For reinforcement modification, all studied reinforcements were inorganic materials, while many types of natural cellulose fiber have received much interest for use as the reinforcement with the benefit of being environmental friendly. In this work, admicellar polymerization was applied in order to modify the natural cellulose fiber for use in natural fiber-polymer composite.

Admicellar polymerization generally consists of three main steps: admicelle formation, monomer adsolubilization and polymer formation as illustrated in Figure 2. The method makes use of the formation of a surfactant bilayer or admicelle on a substrate at a surfactant concentration just below the critical micelle concentration (CMC). In the outer surfactant layer, the amphiphilic molecules are oriented with ionic head groups in contact with the aqueous solution, while the long hydrophobic tails interact to form a hydrophobic inner core. An inner layer oriented with the head groups in contact with the substrate completes the surfactant bilayer. When an organic monomer is added into the system, it will be preferentially adsorbed in the core of the admicelle in a process called "adsolubilization", and when an initiator is added, the monomer in the admicelle will undergo a polymerization reaction to form a polymeric layer on the substrate surface. After the polymerization, surfactant in the upper layer may be removed by washing to expose the polymeric layer on the substrate surface. The polymeric film formation in this process is controlled by several parameters including the characteristics of the substrate surface, the type of surfactant, monomer molecule, the electrolyte and pH. The natural cellulose fiber treatment by admicellar polymerization has already been successfully carried out for other purposes in previous studies, for example, to produce hydrophobic cotton with polystyrene and cross-linked polystyrene coating [14,15]. In addition, both cationic and anionic surfactants have been used [16].

In this work, admicellar polymerization of methyl methacrylate was carried out using hexadecyl pyridinium chloride cationic surfactant. Cationic surfactant was selected because it is expected to be well adsorbed on the negatively charged cellulose in aqueous solution. The reaction of PMMA film formation was initiated by sodium persulfate. The schematic model of PMMA-coated sisal by admicellar polymerization is illustrated in Figure 3. The surface characteristics of admicellar-treated sisal were determined by the flotation test, moisture absorption, ζ potential and point of zero charge (PZC). The hydrophilicity or hydrophobicity of surface can be simply investigated by flotation on water surface and moisture absorption, while ζ potential and PZC can be applied to study the electrokinetical property of the surface. In order to increase the adhesion of cellulose fiber in polymeric composite, the hydrophilicity or high value of ζ potential of the fiber surface must be reduced to approach hydrophobicity or ζ=0 mV, the same as the behavior of polymer matrix of composite. Film formation was analysed by evaluating the weight loss extracted with acetone and chloroform. In addition, thermogravimetric analyses (TGA) was utilized to observe the thermal behaviour and to recheck the weight loss from film formation analysis. The relation between ζ potential and weight loss was established. The effect of surface modification by admicellar polymerization on the thermal stability of sisal fiber with different PMMA contents was evaluated. Moreover, Fourier transform infrared spectrometer (FTIR) and scanning electron microscopy (SEM) were applied for PMMA identification of coated film and morphology study, respectively.

2. EXPERIMENTAL

2.1 Materials

Sisal fibers (0.20-0.22 mm diameter) were obtained from a local source and cut into short fibers 10.0 mm long. Before use, they were washed by 6% NaOH solution at 30°C, 48 h, for wax removal [20] and then placed in an oven at 110°C until dry. Hexadecyl pyridinium chloride (HDPyCl, 98% purity), methyl methacrylate (MMA, 99% purity) and sodium persulfate ($Na_2S_2O_8$, 98% purity) were purchased from SR Laboratory Co. Ltd. Ethanol, hydrochloric acid, sodium hydroxide and potassium chloride were purchased from Merck. All chemicals were used as received.

2.2 Admicellar Polymerization

Admicellar polymerization of PMMA on sisal fibers was carried out in 800 µM HDPyCl solution. The amounts of MMA monomer used were 0.025, 0.05, 0.075, and .1% (V/V) with 0.01, 0.02, and 0.03 g of $Na_2S_2O_8$ respectively. The experiment was performed by following the admicellar polymerization process as shown in Figure 2. At the start of the experiment, 20-g sisal fibers were added into a 1000 mL flask containing 400 mL of the HDPyCl solution. In the first step the system was left for 24 h at room temperature for admicelle formation on the fiber surface. In the second step MMA was added, and the system was left to reach the equilibrium MMA adsolubilization into the core of admicelle at room temperature for 48 h. In the third step initiator was added to the system and the temperature was raised to 60°C to initiate the polymerization reaction of MMA. After 1 h., the system was cooled to room temperature and the treated fibers were removed and washed with distilled water and then extracted with a mixture of 70/30 v/v water/ethanol for 24 h. The extraction step was repeated until the outer layer of surfactant was completely removed as indicated by the absence of foam in washed water. The treated fibers were finally dried in an oven at 60°C for 5 h.

2.3 Surface Behavior

The surface behavior of the untreated and admicellar-treated sisal was investigated to determine the degree of their surface hydrophobicity. For these purpose, flotation, moisture absorption and ζ potential of the fiber were determinded.

In the flotation test, the floating time of the sisal fiber on the water surface was measured. The fiber was judged as completely hydrophobic when it could float for more than 100 min. Figure 4 shows the results of the flotation testes of hydrophilic and hydrophobic surfaces.

To determine the moisture absorption of the fiber, about 3-gram samples were dried in an oven at 100°C until the weight was constant. They were then placed in a room with temperature at 27°C and 65% specific humidity for 24 h. The moisture absorption of the fiber was then measured by the Moisture Analysis Mettler Toledo model LJ 16.

The ζ potential and PZC measurements were also utilized for surface charge study of treated and untreated sisal fibers. The ζ potential was determined in 0.001M KCl-electrolyte solution, using the Laser Doppler Electrophoresis (LDS) model Zetasizar 3000 (Malvern Instrument) and the values were automatically calculated by the Smoluchowski equation [7,21,22]. By measuring the ζ potential as a function of the pH, PZC can be determined.

2.4 Film Formation Analysis

The treated sisal fibers were extracted by two types of solvents, acetone and chloroform, at room temperature for 24 h. The amount of PMMA film formed was calculated from the weight loss by the following equation,

$$\%\ \text{Weight Loss} \quad = \quad \frac{(\text{Weight before extraction} - \text{Weight after extraction})}{\text{Weight before extraction}} \text{x100} \qquad (1)$$

Thermogravimetric analyses (TGA) was also used to determined the amount of PMMA coated on sisal fiber [7]. The experiments were carried out on Netzsch model STA 409C over the temperature range from 30°C to 450°C with a heating rate of 5°C/min under nitrogen atmosphere. One mg sample was used for each experiment. The amount of PMMA coated on fiber surface was determined from the weight loss before and after degradation of PMMA according to equation 2.

$$\% \text{ Weight Loss} = \frac{(\text{Weight before deg radation} - \text{Weight after deg radation})}{\text{Weight before deg radation}} \text{x} 100 \qquad (2)$$

2.5 Film Identification and Morphology Study

The PMMA film formed on the sisal fiber surface was identified by Fourier transform infrared spectrometer (FTIR), Perkin Elmer Model 2000, using the KBr disc technique.

The scanning electron microscopy (SEM) micrographs of the untreated and admicellar-treated fibers were taken by Jeol SEM model JSM 5200. Before taking their micrographs, they were coated with gold in a sputter coater under vacuum.

3. RESULTS AND DISCUSSION

3.1 Hydrophobicity Behavior by Flotation Test and Moisture absorption.

The hydrophobicity of untreated and treated sisal fibers by flotation test is shown in Figure 4. The admicellar-treated sisal fibers floated on the water surface for more than 100 min, whereas the untreated sisal fibers gradually sinked to the bottom as soon as they were placed on the water surface. The results indicated that the sisal surface was completely changed from hydrophilic to hydrophobic surface after treated by the admicellar polymerization technique. The floating time of admicellar-treaded sisal fibers depended on the amount of monomer and initiator used in the system as shown in Figure 5. It was found that the higher the amount of monomer and initiator added, the longer the floating time up to the saturation point. When using MMA of 0. 075% by volume, the floating time reached a constant value. This meant that 0. 075% by volume MMA was sufficient for PMMA film formation on the fibers surface when the system had the proper quantity of initiator using sodium persulfate.

The moisture absorption of the treated sisal fibers is shown in Figure 6. The results show that the moisture absorption of the treated sisal fibers decreased with increasing amounts of the MMA monomer and $Na_2S_2O_8$ initiator up to 0.075% volume of MMA, after which there was no significant change. The results are consistent with the flotation tests described previously. Through admicellar polymerization, the moisture absorption of the sisal fibers was found to decrease from the original value of 7.98 % to 4.48%.

3.2 Surface Electric Charge by ζ Potential and PZC

ζ Potential and PZC of untreated and admicellar-treated sisal fibers and PMMA are shown in Figure 7. The PZC can be determined from the pH at which ζ potential = 0. The PZC of untreated sisal was found to be 2 whereas the PZC of the admicellar-treated sisal was 3.5, which is close to the PZC of PMMA of 3.8. In the neutral aqueous solution (pH 7), the ζ potentials of untreated sisal, admicellar-treated sisal and PMMA were approximately -17, -11 and -10 mV, respectively. This study shows that the electrokinetical surface of sisal fiber coated with PMMA clearly changed from that of the untreated sisal to become closer to the electrokinetical surface of PMMA. Moreover, this experiment can help to decide the appropriate condition for the admicellar polymerization process in which surfactant adsorption can be increased using a pH higher than the PZC of untreated sisal when a cationic surfactant is used.

The changes in ζ potential at pH 7 and PZC of sisal fibers treated with varying amount of monomer and initiator are shown in Figure 8 and 9, respectively. The results show that the polymeric film coated on the fiber surface had the influence to increase the ζ potential and PZC with increasing amount of monomer and initiator until the polymeric film completely covered the fiber surface at around 0.075% by volume of MMA. It is interesting to note that the results of ζ potential and PZC measurement are entirely consistent with changes in hydrophobicity of the fibers described in 3.1.

3.3 Film Formation Analysis

In order to investigate the amount of film formed on the fiber surface, the weight loss of the treated fiber by solvent extractions was determined. Two different types of solvents, acetone and chloroform, were used for comparison and confirmation of this study. The experiment can also confirm the results of the ζ potential, which is related to the amount of film on the surface. The results are shown in Figures 10 and 11. The weight loss from both extracting solvents had the same tendency while chloroform gave slightly higher figures due to the higher solubility of PMMA. The results show that PMMA film formation reached saturation when using 0.075% by volume MMA which is in agreement with the change in ζ potential.

TGA was carried out in order to evaluate the effect of surface treatment on the thermal stability of sisal fibers with different PMMA contents. Figure 12 shows thermograms for (a) untreated sisal fiber, (b), (c), (d), (e) correspond to admicellar-treated sisal fibers using 0.03 g initiator with 0.025%, 0.050%, 0.075% and 0.10% by volume of MMA, respectively, and (f) PMMA. It can be observed that PMMA is more thermally stable than untreated and all treated fibers, while the treated fibers are slightly more stable than the untreated fiber. The degradation temperature of treated fibers also increased as PMMA content increased and the treated fibers with 0.075% and 0.100% by MMA volume have similar behavior. The weight loss of the sisal fiber in lines b to d over the temperature range of 350 to 400 ^{o}C which is the degradation temperature of PMMA as shown in line f was also estimated.

3.4 The Relation of Zeta Potential and Film Formation

The data of ζ potential and weight loss analysed with acetone and chloroform extraction and TGA of PMMA film on sisal surface show good linear relationship as shown in Figures 13 and 14, respectively.

3.5 FTIR Identification of PMMA Film and SEM Morphology of Sisal Surface

PMMA film coated on sisal fiber was identified by FTIR. Figure 15 shows the FTIR spectra of (a) PMMA, (b) untreated sisal, and (c) admicellar-treated sisal. The spectrum of the admicellar-treated sisal fiber shows the key characteristic peaks of PMMA with the peak of carbonyl (C=O) group at 1733 cm^{-1} and methyl group at 1149 cm^{-1}, whereas the spectrum of the bare sisal fiber has the characteristic peaks of the hydroxyl and carboxyl groups at 3421 and 1051 cm^{-1} respectively. These results clearly indicated that PMMA was successfully formed on sisal surface by admicellar polymerization in HDPyCl cationic surfactant system.

In order to verify the presence of PMMA film treated on sisal fiber, the SEM micrographs of the untreated fiber and admicellar-treated fiber surfaces were taken as shown in Figure 16. Comparison between the untreated fiber (Figure 16a) and treated fiber (Figure 16b) images shows that the two surfaces were quite different. The admicellar-treated sisal showed a thin film coated on the sisal surface. This confirms the presence of PMMA coated on the surface of treated sisal fiber.

4. CONCLUSIONS

The formation of PMMA film on sisal fiber surface by admicellar polymerization was successfully carried out in the HDPyCl-MMA-sisal system using sodium persulfate as an initiator. The amount of MMA and initiator had the effect on the amount of film coverage on the surface. The surface coating reached saturation with PMMA at 0.075% by volume and with 0.03 g sodium persulfate. Moreover, hydrophobic character of the admicellar-treated sisal was confirmed by the floating time, moisture absorption, and surface charge measurements. The amount of film formation in terms of weight loss evaluated by solvent extractions and TGA show the linear relation with the values of ζ potential. The presence of PMMA film coating on the sisal fiber surface was also confirmed by FTIR analysis and SEM micrographs.

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List of Table

Table 1. Chemical compositions and mechanical properties of sisal fiber [2]

Chemical composition	
Cellulose (%)	67 – 78
Lignin (%)	8.0 – 11.0
Hemicellulose (%)	10.0 – 14.2
Moisture content (%)	11.0
Mechanical properties	
Tensile strength (MPa)	468 – 640
Young's modulus (GPa)	9.4 – 22.0
Elongation at break (%)	3 – 7

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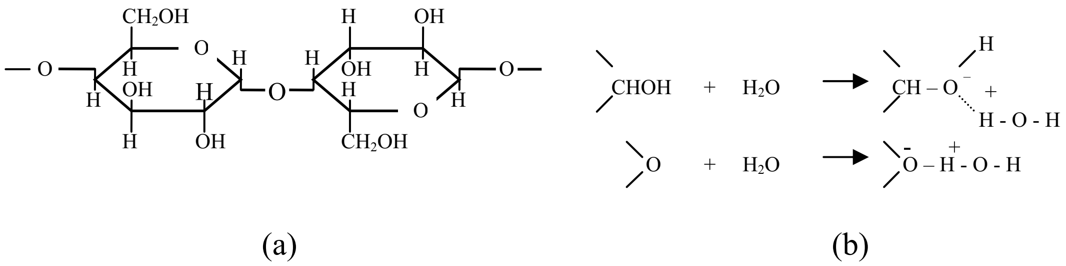
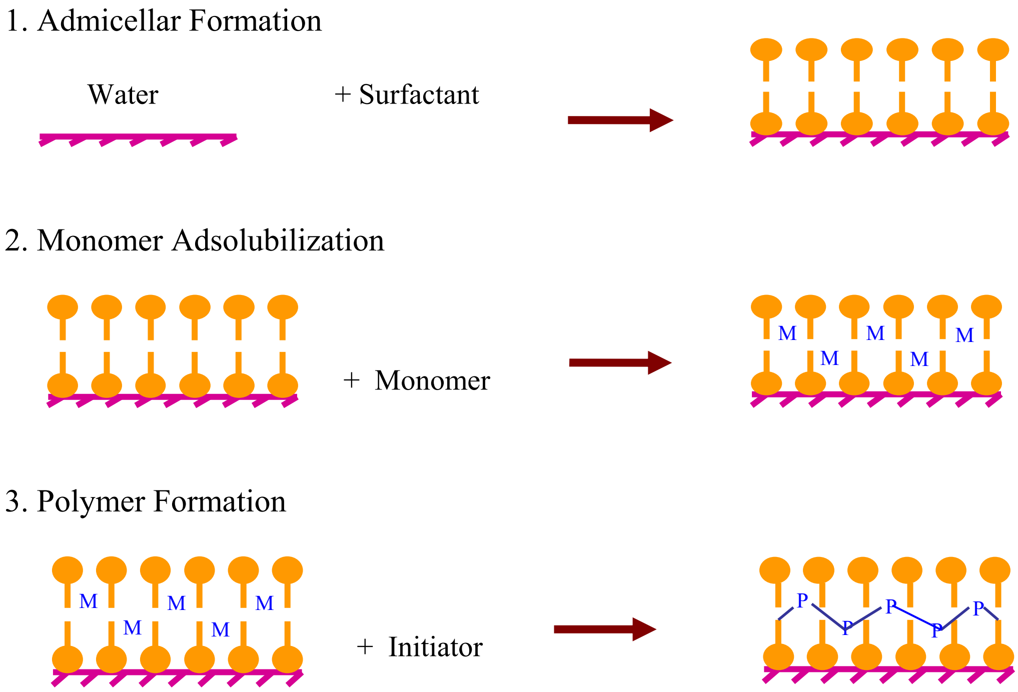


Figure 1. Cellulose structure: (a) chemical structure and (b) interactions with water molecules.



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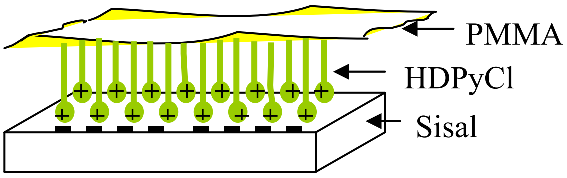

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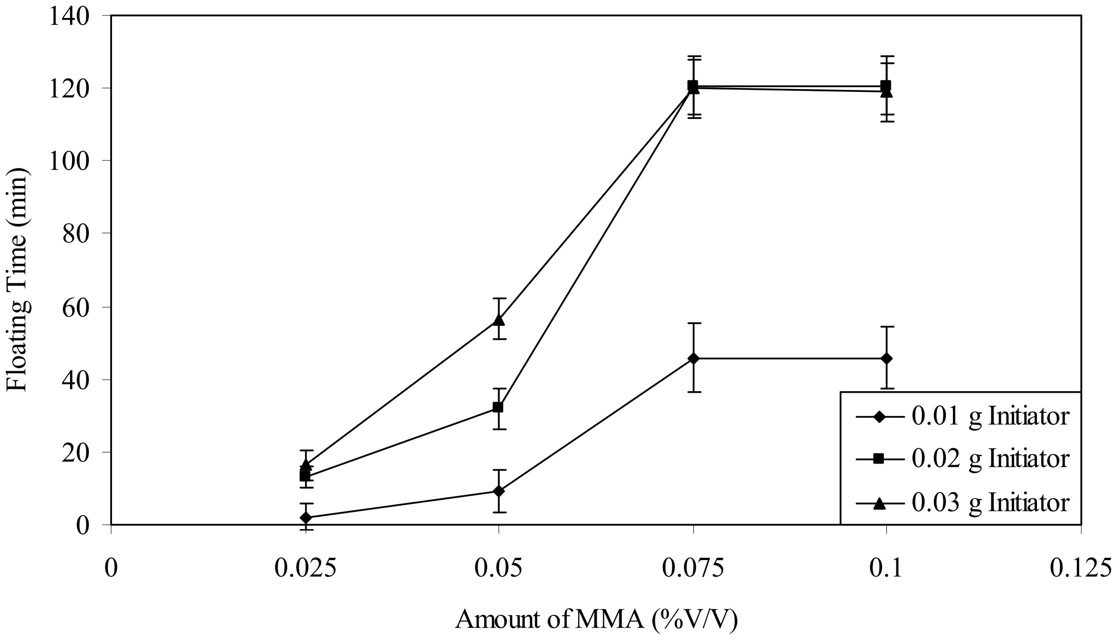

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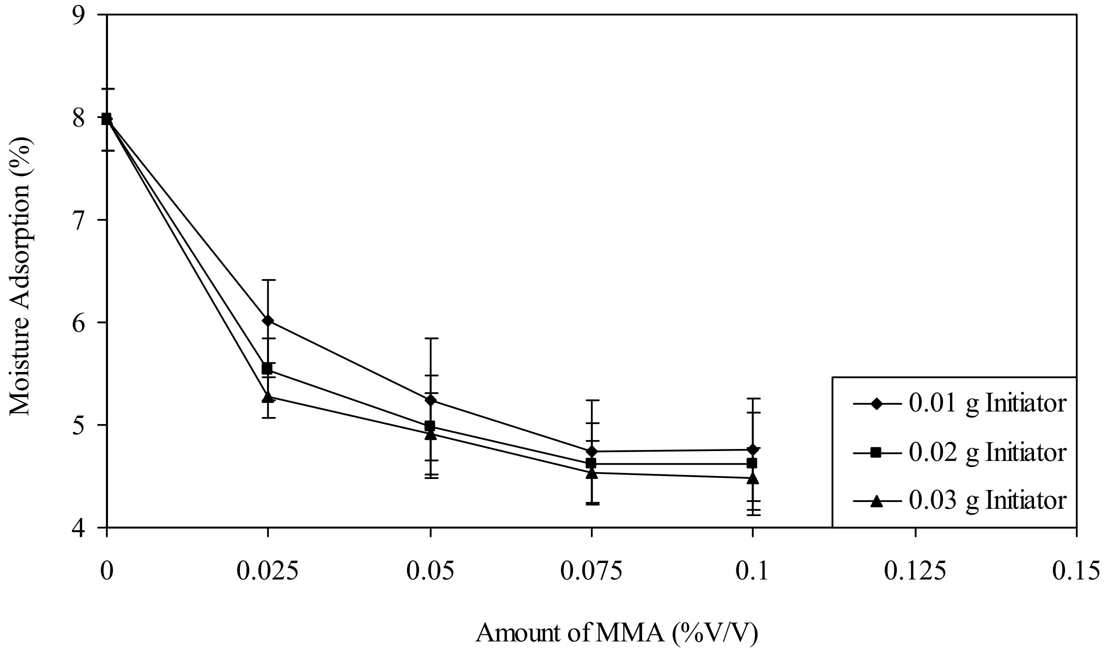

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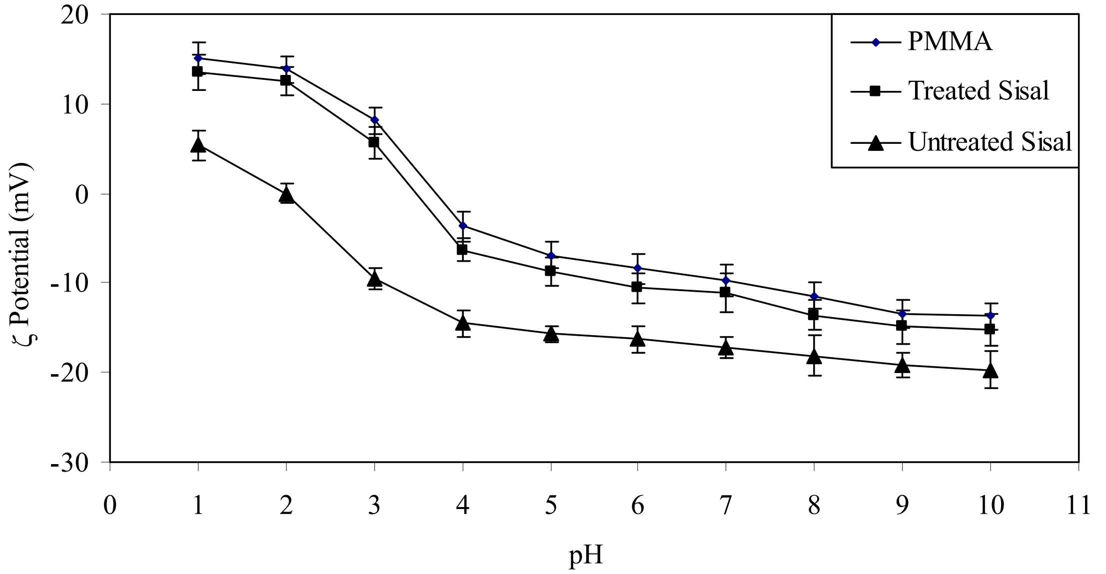

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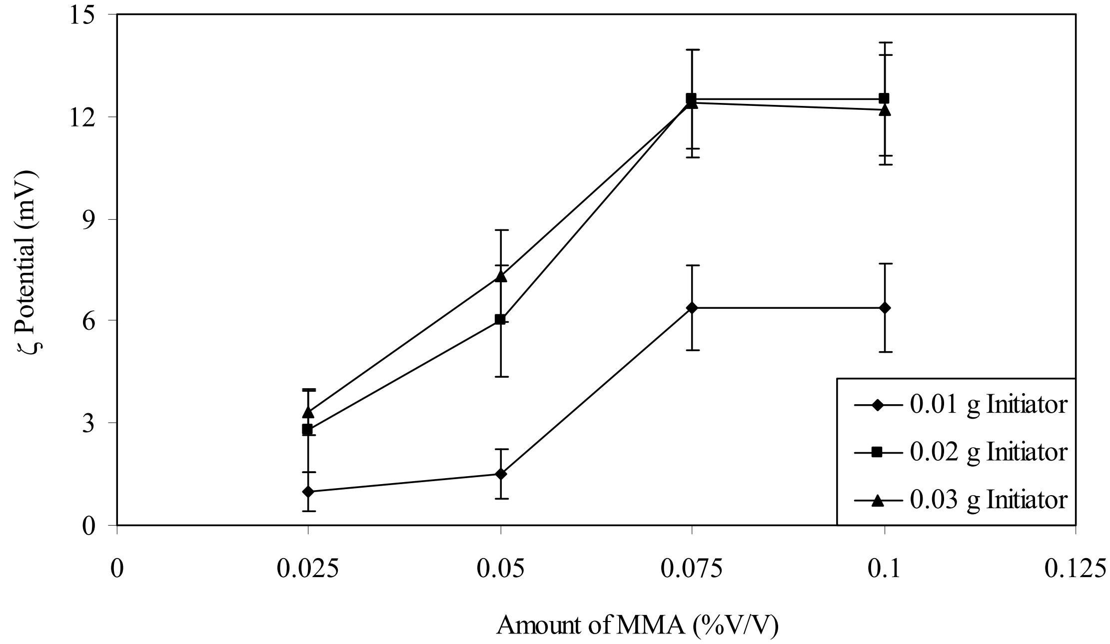
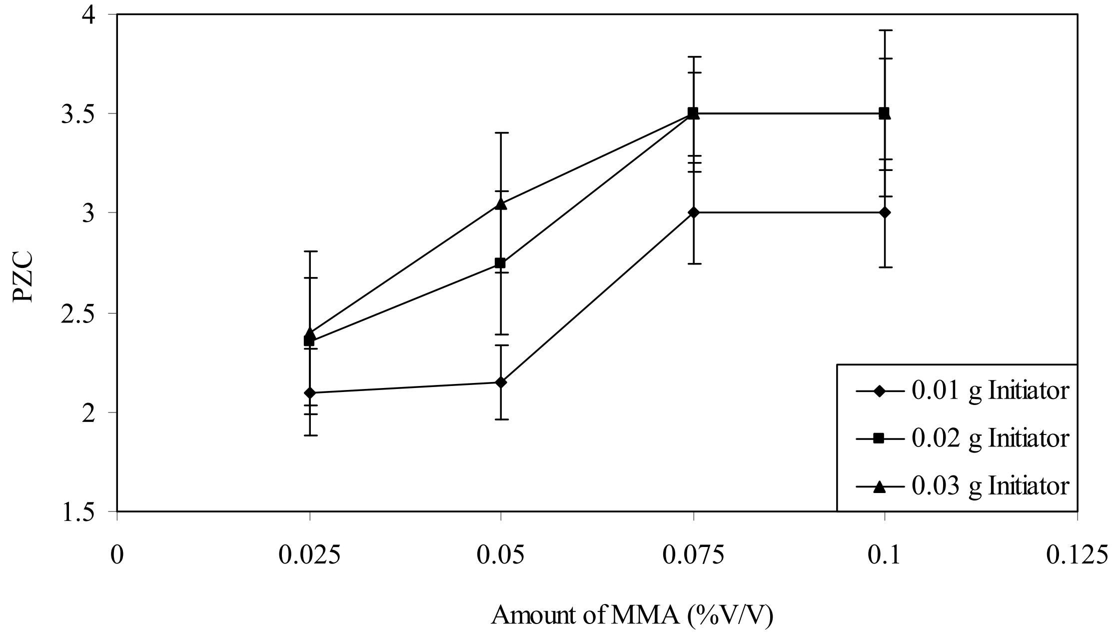


Figure 8. The ζ potential of the admicellar-treated fibers using different amounts of MMA and initiator.



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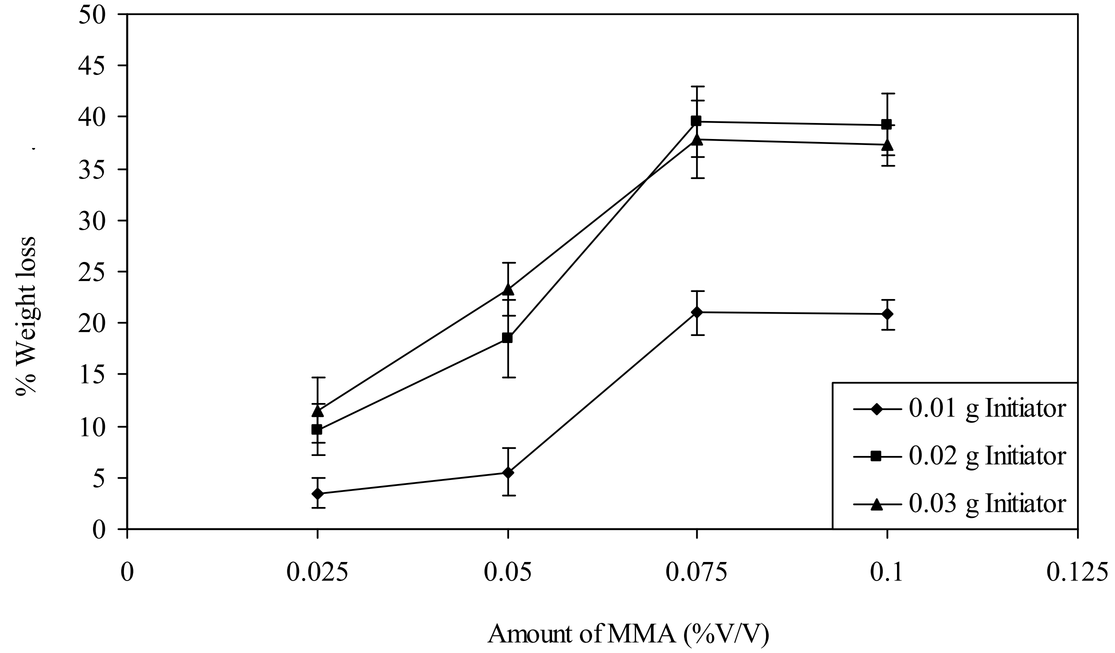

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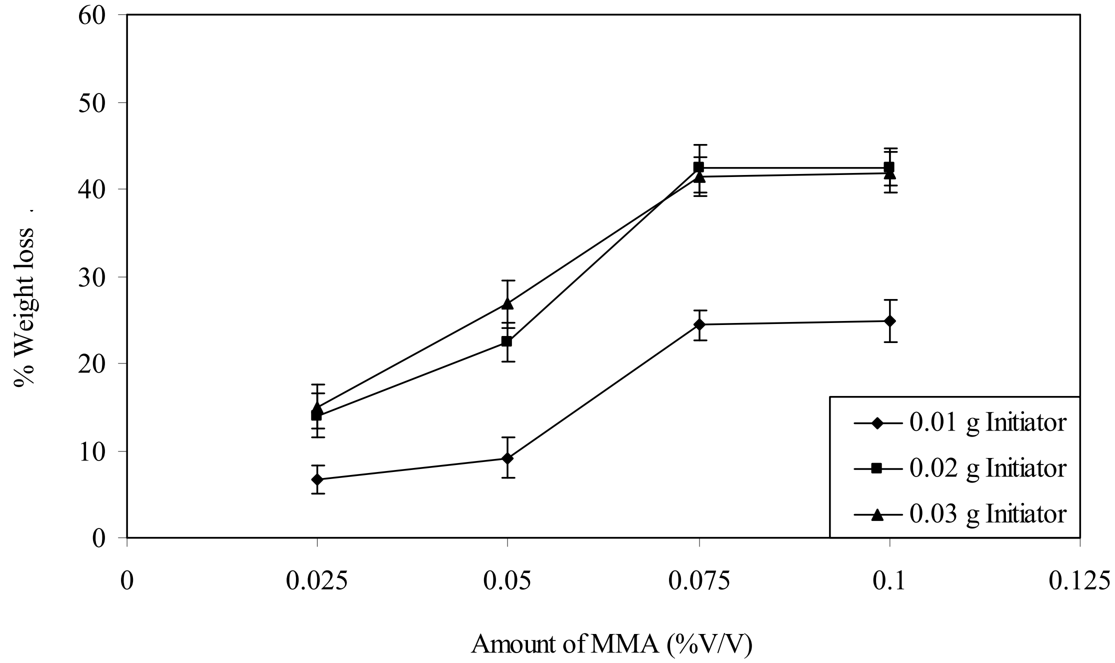

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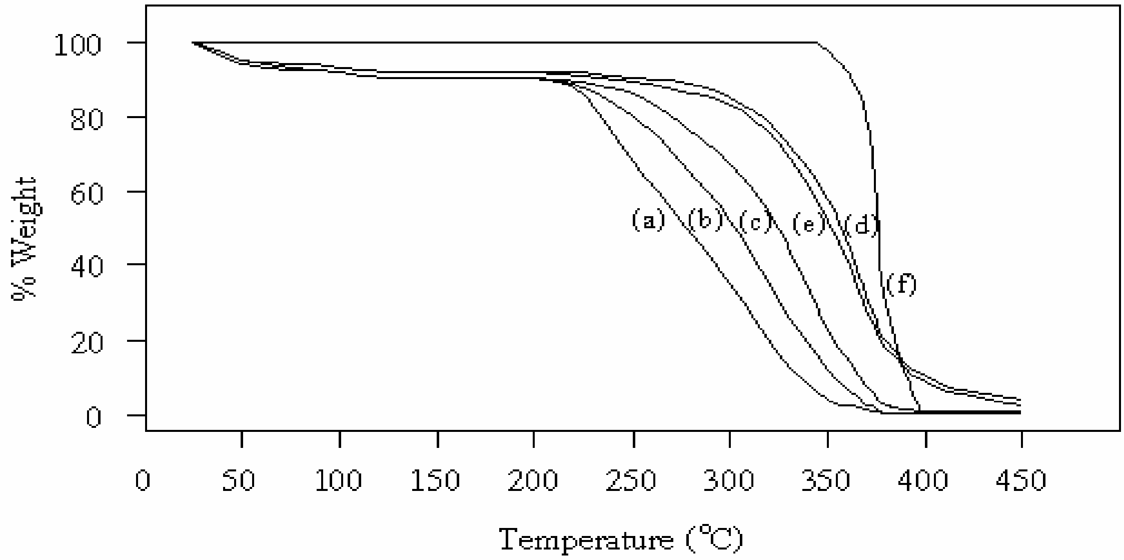

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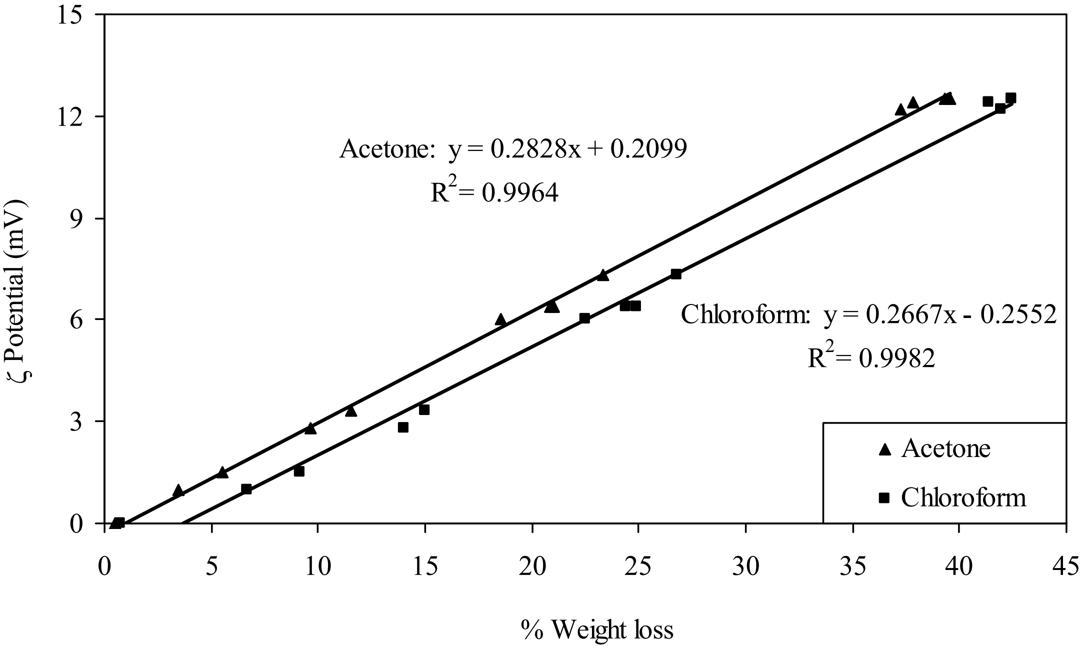

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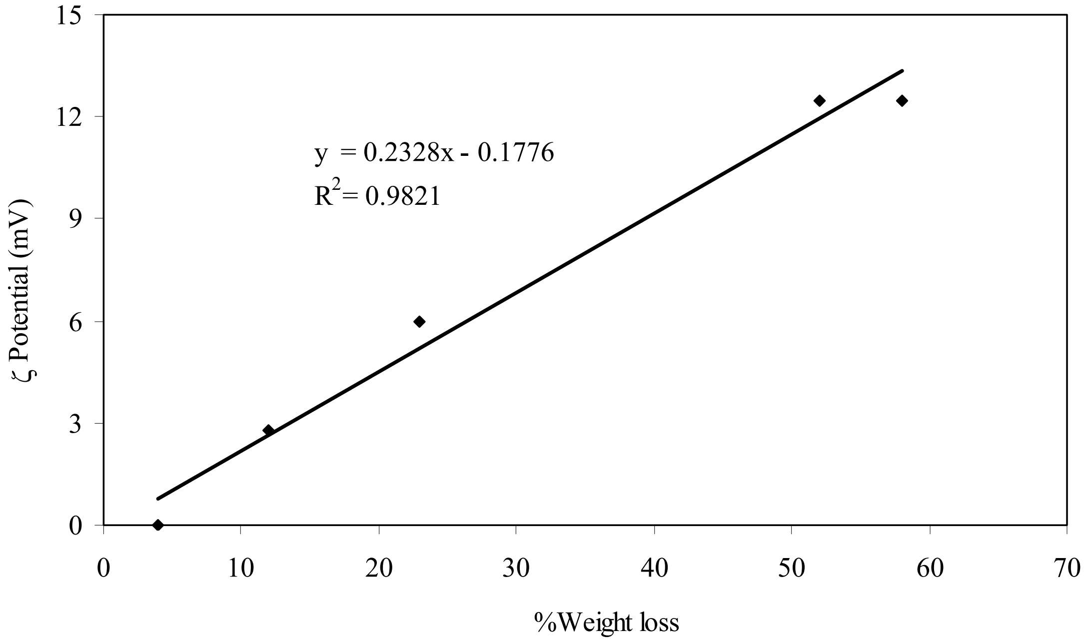

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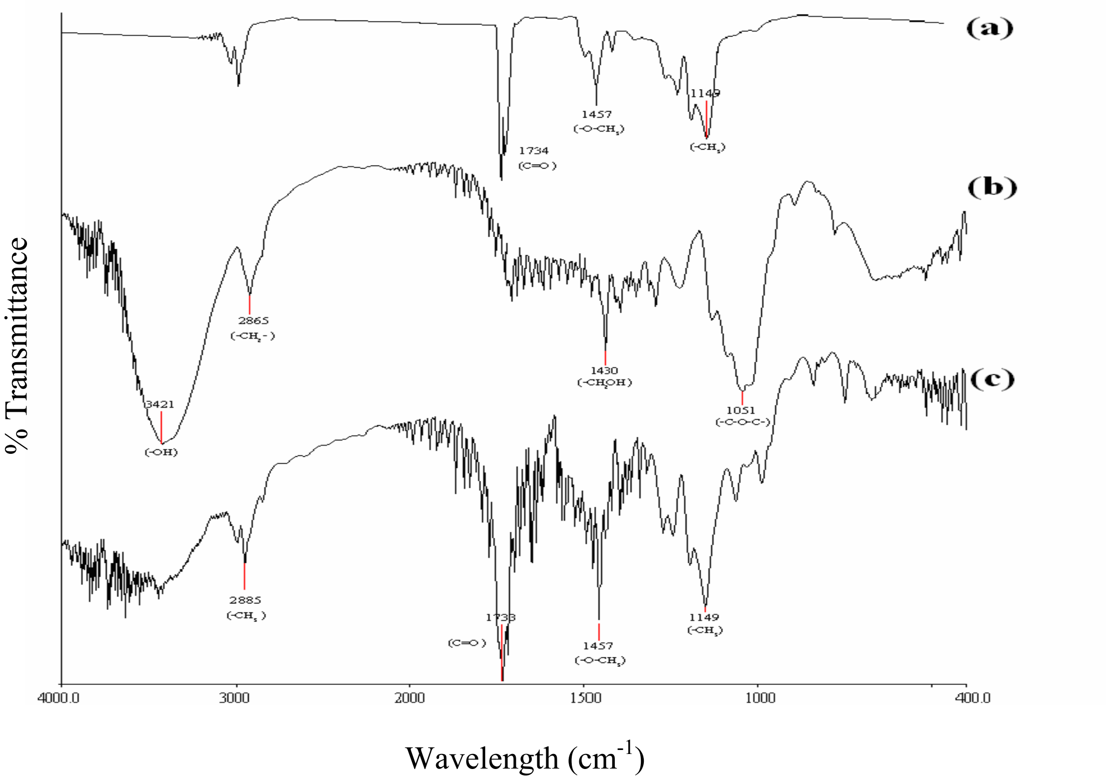

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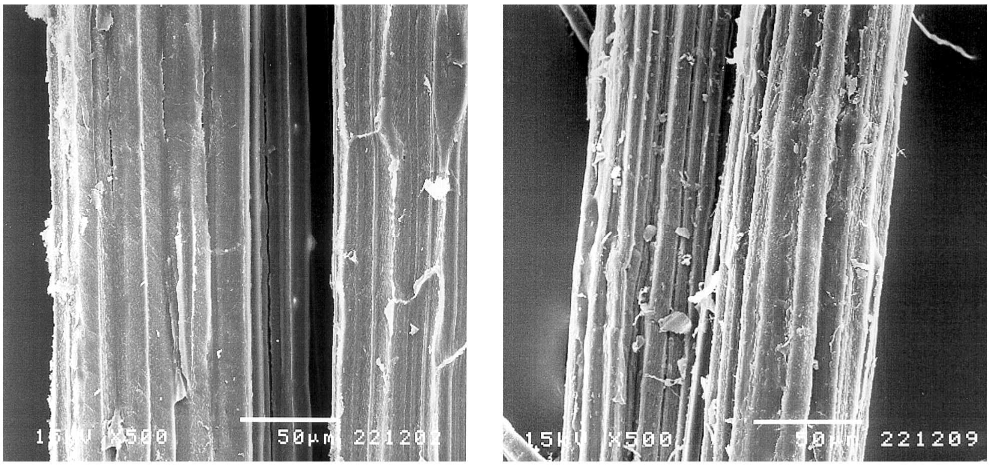

(a) (b)

Figure16. SEM images of (a) untreated sisal fiber and (b) admicellar-treated sisal fiber.

Mechanical Property Improvement of Unsaturated Polyester Composite with Admicellar-Treated Sisal Fibers

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Abstract

Sisal fiber was treated by admicellar polymerization with poly(methyl methacrylate) film coating in order to enhance the interfacial adhesion of the fiber/polymer composite for mechanical property improvement. The surface characteristics of admicellar-treated sisal fiber were investigated by moisture absorption and electrostatic charge. Thermal stability (by thermogravimetric analysis) and film identification (by Fourier transform infrared spectroscopy) were also investigated. The treatment was shown to improve the tensile and flexural properties, impact strength, and hardness. The morphology of the tensile fracture surface of sisal/unsaturated polyester composites was pictured by scanning electron microscopy to considerate the interfacial adhesion improvement of the composite.

Keywords: sisal fiber surface treatment, admicellar polymerization, reinforced unsaturated polyester composite, mechanical property

1. Introduction

The mechanical properties of plant fiber-polymer matrix composite are controlled to a large extent by the efficiency of a bonding at the fiber-matrix interfacial boundary. The principle function of the interface is to facilitate transfer of stress from fiber to fiber, across the matrix. Cellulose fiber is however known to exhibit poor bonding characteristic with polymeric matrix. This is mainly due to the presence of organic and inorganic substance on the fiber surface and the hydrophilic nature of cellulose, which prevents direct contact between the molecules of the fiber and the polymer matrix. The surface of plant fiber such as sisal fiber is usually not suitable for creating a strong bond with a polymeric matrix. The bond strength has been successfully improved by modifying the fiber surface with several methods for chemical or physical surface treatment.

Sisal fiber is one of the most widely used plant fibers. Sisal fiber is obtained from the leaves of *Agave Sisalana* plant that is largely available in the tropical zone countries. During the past decade, the sisal fiber has raised great interest to use as an economical and environmental friendly reinforcement for polymeric composite. To improve the interfacial adhesion of fiber/polymer composite, sisal fiber must be treated from hydrophilic surface to be hydrophobic surface. There have been many researchers applying several techniques in order to develop natural cellulose fiber surface that has been reported [1-9]. A special review of sisal fiber treatment for the development of the mechanical properties of its composite has been concluded by Y. Li and *et al* [1]. For using sisal fiber as a reinforcement in the polymeric composite, unsaturated polyester is a popular thermoset used as a polymer matrix. P.A. Sreekumar and *et al* studied the mechanical properties of sisal fiber-reinforced polyester composite [9]. They deeply observed the tensile and flexural behavior of sisal fiber/polyester composite as a function of fiber length and fiber loading. The surface characteristics of natural fiber are also the attractive factor for researchers in order to develop the adhesion of natural fiber/polymer composite. To investigate the hydrophobicity of fiber surface, several techniques such as wetting and spreading phenomena, moisture absorption, and electrostatic charge have been used [2, 9, 10-12]. In present study, admicellar polymerization was used in order to develop sisal fiber surface for interfacial adhesion improvement of sisal fiber/unsaturated polyester composite. The surface characteristics of the admicellar-treated sisal fiber and the mechanical properties of the treated sisal fiber composite were investigated to describe that admicellar polymerization had the effectiveness to develop the bonding of the natural fiber/polymer composite.

Admicellar polymerization is an innovative technique used to develop material surface with ultrathin film of proposed polymer. Admicellar polymerization generally consists of three main steps: admicelle formation, monomer adsolubilization and polymer formation. After the polymeric film formation, the upper layer of surfactant must be removed to expose the layer of polymer on the substrate surface. The mechanism of admicellar polymerization is shown in Figure 1. The polymeric film formation of this process is controlled by several parameters including the characteristic substrate surface, the type of surfactant, monomer molecule, condition of pH and electrolyte. Admicellar polymerization has been applied to improve the interfacial adhesion of the reinforced polymer composite by forming different polymers on the different reinforcements such as, precipitated silica with polystyrene [13] and copolymer of styrene-butadiene and styrene-isoprene [14], glass fibers with polystyrene [15] and copolymer of isoprene-styrene [16]. In previous work, admicellar polymerization was used for inorganic reinforcement. This study is the first one that applied admicellar polymerization to develop the plant fiber surface for using as the reinforcement for polymeric composite. Previously, admicellar polymerization has been applied to modify cellulose fiber surface such as coating PMMA on cellulose fiber [17], and coating polystyrene on cotton [18]. Moreover, the cross-linked polymer film formation has also been carried on by admicellar polymerization such as, cross-linked polystyrene on cotton [19] and cross-linked polystyrene on alumina particle [20]. Not only for polymeric composite application, but for other fields, admicellar polymerization has also been applied such as, producing hydrophobic cotton [18-19], developing natural rubber latex [21], coating mica with electropolymer [22], and protecting the corrosion of aluminium [23].

In this work, the sisal fiber surface was treated by admicellar polymerization using hexadexyl pyridinium chloride as surfactant to form PMMA film for enhancement of the sisal fiber/unsaturated polyester matrix composite adhesion. Surface characteristics of the admicellar-treated sisal fiber and mechanical properties of the composite have been investigated.

2. Experimental

2.1 Materials

Sisal fibers (diameter 0.22-0.27 mm) were obtained from a local source. Hexadexyl pyridinium chloride (HDPyCl, 98% purity), methylmethacrylate (MMA, 99% purity) and sodium persulphate (98% purity) were purchased from SR Laboratory Co.Ltd.. Unsaturated polyester resin (UP) was purchased from ……, Cobaltnapthanate and Methyl ethyl ketone peroxide (MEKP) were supplied by Merch.

2.2 Sisal surface treatment by admicellar polymerization.

The sisal fibers were preliminary treated by alkali treatment with soaking in 6% NaOH at 30°C for 48 h. Then they were washed and put in oven at 110°C until dry.

After alkali treatment, 20-g sisal fibers were chemically treated by admicellar polymerization using 100 μM HDPyCl solution. The amount of MMA monomer was varied of 0.025, 0.05, 0.075, and 0.1% by volume with $Na_2S_2O_8$ initiator of 0.02 g into 400-ml HDPyCl solution. In the experiment, the system was carried with the three main steps of admicellar polymerization, admicellar formation, adsolubilization, and in-situ polymerization as shown in Figure 1. The first step was performed for 24 hr at room temperature to reach the equilibrium of surfactant adsorption onto the sisal fiber surface. Then MMA was added to the system and left to reach the equilibrium of MMA solubilization into the core of admicelle at room temperature for 48 h. The initiator was added to the system and the temperature was raised to 60°C for the polymerization reaction of MMA for 1 h. After that the system was cooled down to room temperature.

Then the treated fibers were washed with distilled water and extracted with the mixture of 70/30 v/v water/ethanol for 24 h. Finally the treated fibers were dried in an oven at 60°C for 5 h.

2.3 Reinforced unsaturated polyester composite preparation

The admicellar-treated sisal fibers coated with PMMA and untreated fibers were chopped to the desired length of 10, 20, 30 and 40 mm using as a reinforcement for composite preparation. Unsaturated polyester resin was mixed with 1 wt% cobaltnapthanate (accelerator) and 1 wt% methyl ethyl ketone peroxide (curing agent) for matrix preparation of composite. Composite sheets were made by hand lay up technique using a stainless steel mold in the dimensions of 13x17x0.3 cm. Polyvinylalcohol (releasing agent) was coated onto the surface mold before laying the matrix and the fibers into the mold. The desired fiber loading (10, 20, 30 and 40 vol%) of the desired fiber length was laid and 70-ml unsaturated polyester resin was poured onto the fibers into the mold. The mold was closed and then the mixture was left to cure for 12 h at room temperature [8].

2.4 Fiber surface characterization

The surface characterization of admicellar-treated and untreated sisal fibers was investigated by measuring moisture absorption and electrostatic surface charge to observe the surface hydrophobicity. Moreover, thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR) were applied to analyze and identify PMMA film on sisal surface.

Moisture absorption of the treated and untreated fibers was observed by placing 3-g dried fibers under the room conditions with 27°C temperature and 65% specific humidity overnight. After that Moisture Analysis Mettler, Toledo model LJ16, was used for moisture absorption measurement. Surface charge of fibers was determined by zeta (ζ) potential measurement using Laser Doppler Electrophoresis (LDS), Malvern model Zetasizar 3000. The measurement was done in 0.001M KCl-electrolyte solution.

The thermal behavior of the sisal fibers was investigated by TGA, NETZSCH STA 409C, over the temperature range from 30°C to 450°C with 5°C/min heating rate under nitrogen atmosphere. For each experiment, about 1-mg sisal fiber samples were performed. PMMA film formed on sisal fiber surface was also identified by FTIR, Perkin Elmer Model 2000, using the KBr disc technique.

2.5 Mechanical property testing.

Tensile and flexural tests of the composite samples were carried out on an Universal Testing Machine model LR 10K according to the standard test of ASTM D638 and D790 respectively. Five samples were tested in each experiment. Tensile strength and modulus were conducted using dumbbell shape specimens of 115 mm in length with a crosshead speed of 10 mm/min and a gauge length of 50 mm. For flexural tests, rectangular test specimens of 62x12.7x3 mm dimension were used with a crosshead speed of 1.28 mm/min in a three-point loading, fitted by a 100 kN load cell.

Impact tests were performed on an Izod Impact model 258-D in according with ASTM D256. Five rectangular test specimens with dimensions of 62x12.7x3 mm were used. Hardness tests were performed on a Durometer Type D in according with ASTM D2240. The rectangular test specimens, 13x17x0.3 mm dimension, were used.

2.6 Morphology study of the sisal fiber composites

The cross-section surface of the sisal fiber composite specimens after tensile testing were pictured and observed by scanning electron microscopy (SEM), the Joel SEM 5200. The adhesion between the sisal fiber and polymeric matrix were explained from their SEM micrographs.

3. Results and Discussion

3.1 Surface development by admicellar polymerization.

3.1.1 Surface behavior.

The hydrophobicity of the admicellar-treated sisal fiber surface was investigated by moisture absorption and ζ potential measurement. The moisture absorption of the sisal fibers was dramatically reduced through increasing the amount of MMA monomer as shown in figure 2. The moisture absorption was reduced from 7.98% to 4.48% of the lowest studied value of admicellar-treated sisal by 0.1% by volume MMA and 0.02 g $Na_2S_2O_8$. However, the reduction of moisture absorption using 0.075 and 0.1 % MMA volume was not significantly different. The ζ Potential of the untreated admicellar-treated sisal fibers was studied to confirm the changed surface. The ζ potential of untreated sisal, admicellar-treated sisal and pure PMMA was observed by varying pH of 1-10 as shown in Figure 3. It shows that the trend line of admicellar-treated sisal using 0.075% MMA volume and 0.02-g $Na_2S_2O_8$ was closer to the trend line of PMMA. The pH points of ζ potential = 0 of PMMA and admicellar-treated sisal were also closer that they were 3.8 and 3.5 respectively, whereas that of untreated sisal was 2.

The investigation of changed ζ potential at pH 7 of the admicellar-treated sisal by various amount of MMA was shown in Figure 4. These results confirmed the moisture absorption study that the hydrophobicity of the admicellar-treated sisal increased with increasing amounts of MMA monomer until PMMA film formation reached to the saturation at about 0.075 % MMA volume by using 0.02-g $Na_2S_2O_8$ initiator.

3.1.2 Coated film characterization

TGA were carried out in order to analyze the coated film and evaluate the effect of MMA amounts using in admicellar polymerization system on the thermal stability of the treated sisal as shown in Figure 5. It was found that the thermal stability of the treated sisal fiber was higher than that of untreated sisal fiber and it was closer to the thermal stability of pure PMMA that was the expected polymeric film coated on sisal fiber. The thermal stability increased as PMMA content increased when using higher MMA amounts.

PMMA film coating on sisal fiber was also identified by FTIR. Figure 6 shows FTIR spectrums of pure PMMA, untreated sisal fiber and admicellar-treated sisal fiber. The admicellar-treated sisal fiber spectrum, 6(c), shows the characteristic peaks of PMMA at 1734 cm^{-1} and 1457 cm^{-1}, similar to the peaks of pure PMMA, 6(a), whereas the spectrum of the bare sisal fiber, 6(b), has the characteristic peaks at 3421 cm^{-1} and 1430 cm^{-1}. These results clearly indicated that PMMA film was successfully coated on sisal fiber surface by admicellar polymerization.

3.2 Mechanical Properties of Composite.

3.2.1 Effect of the fiber loading of the treated and untreated sisal fibers

The mechanical properties (tensile, flexural, impact and hardness) of reinforced unsaturated polyester composites were investigated by varying the untreated and admicellar-treated sisal fiber loading as shown in Figure 7-10, respectively.

Figure 7 shows the tensile strength (7a) and tensile modulus (7b) of different loading through the MMA amounts in admicellar polymerization treatment. It was observed that both tensile properties increased with increasing of fiber loading up to 30 vol% and the tensile properties slightly decreased at 40 vol% fiber loading of all types of sisal fibers. The treated sisal fiber gave higher tensile properties with higher PMMA film contents coated on sisal fiber surface from various MMA amounts. The flexural properties were also investigated as shown in Figure 8, flexural strength (8a) and flexural modulus (8b). The results show the same trend with the tensile properties. From both studies, tensile and flexural properties, it could be concluded that the optimum fiber loading was at 30 vol% for all sisal fiber types. These results were also observed in the same trend studied by P.A. Sreekumar *et al* [9]. It could be described that at the lower fiber loading, dispersion of fiber is very poor so that stress transfer does not occur property, whereas at the higher fiber loading, there is a strong tendency for fiber-fiber interaction that leads to poor wetting between fiber and polymeric matrix. The treated sisal fiber with higher content of film coating helps improve the fiber-matrix adhesion.

Figure 9 and 10 show the impact strength and hardness of the sisal/unsaturated polyester composites. It was observed that both impact and hardness properties increased with increasing fiber loading. The higher amounts of MMA using gave higher impact and hardness properties.

Based on these results, at the condition using 0.075 vol% MMA, PMMA film could be the saturated point of film formation that shows the insignificant difference of mechanical properties of their composites when using higher MMA amounts and this conclusion was confirmed by fiber surface behavior studied.

3.2.2 Effect of the fiber length of the treated and untreated sisal fibers

The effect of fiber length of untreated and admicellar-treated fibers on the mechanical properties was also investigated as shown in Figure 11-14. The fiber length was varied from 10-40 mm.

The results of tensile and flexural properties are shown in Figure 11 and 12, respectively. These show that the tensile and flexural properties in both strength and modulus increased with increasing fiber length of all sisal fiber types, untreated and admicellar-treated sisal fibers. The maximum value of the properties was obtained at 30-mm fiber length. Further increase in fiber length, showed the decreasing trend in properties. P.A. Sreekumar *et al* [9] also reported a similar trend. It was noted that at higher length, the void of fiber-to-fiber contact was more because of fiber curling and bending that lead to poor resin penetration between into the void. It could be described that effective stress transfer of the fiber-to-matrix interaction is not possible. The results also show that the tensile and flexural properties of admicellar-treated sisal fibers increased with the increase in MMA concentrations due to the adhesion improvement between sisal fiber and unsaturated polyester matrix.

Figure 13 and 14 shows the impact strength and hardness of the sisal fiber composites. It was observed that the impact and hardness properties very slightly increased with increasing fiber length. The admicellar-treated sisal fibers can improve the interaction between the fiber and matrix leading to increase the impact and hardness of the composites.

3.3 Interfacial adhesion of sisal/unsaturated polyester composite

The improvement of interfacial adhesion between the sisal fibers and unsaturated polyester matrix can be clearly seen by SEM micrographs of the tensile fracture surface as shown in figure 15. With a weak interfacial bond, the fracture is more likely to lead to interfacial debonding and extensive fiber pullout as shown in the Figure 15a of untreated fiber composite. If bonding is strong, the failure made is fiber breakage at the fracture point as shown in the Figure 15b of the admicellar-treated fiber composite.

4. Conclusion

This observation can conclude that PMMA film coating on sisal fiber surface by admicellar polymerization leaded to improve the mechanical properties of sisal fiber/unsaturated polyester composite due to the improvement of the interfacial adhesion of the composite.

5. Acknowledgement

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6. Reference

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List of Figure

Figure 1. Mechanisms of admicellar polymerization technique.

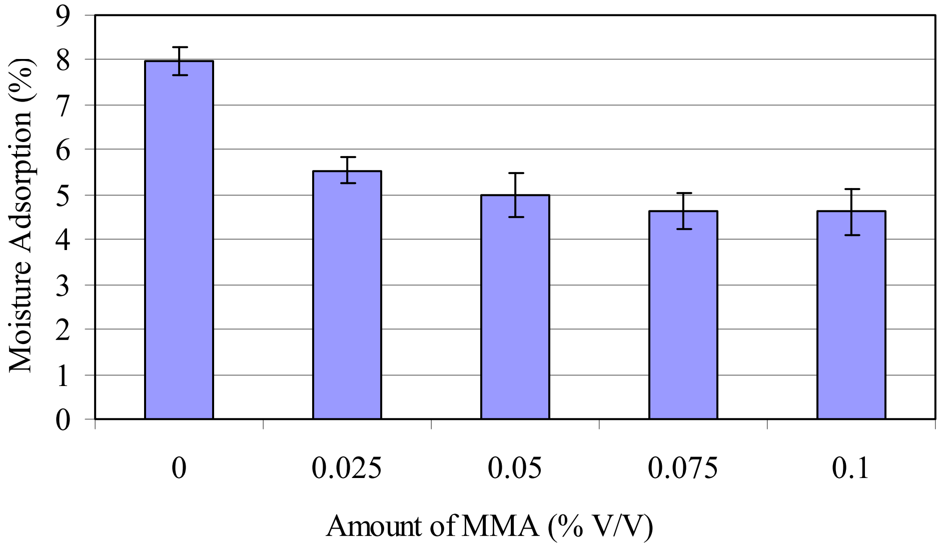


Figure 2. The moisture absorption of the admicellar-treated fibres with various amounts of MMA at 0.02 g $Na_2S_2O_8$.

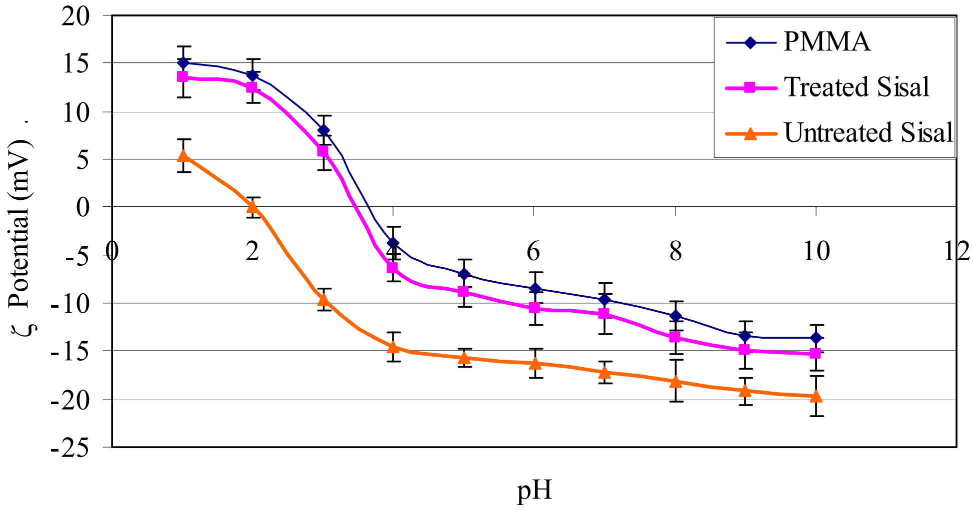


Figure 3. The ζ potential through various pH of untreated fiber, admicellar-treated fiber, and PMMA.

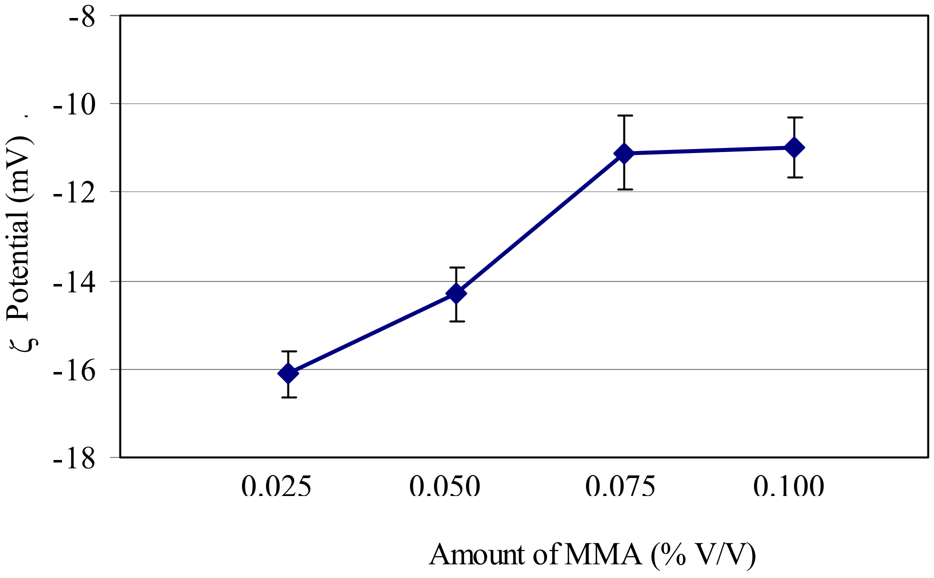


Figure 4. The ζ potential at pH 7 of the admicellar-treated fiber with various amounts of MMA by using 0.02 g $Na_2S_2O_8$.

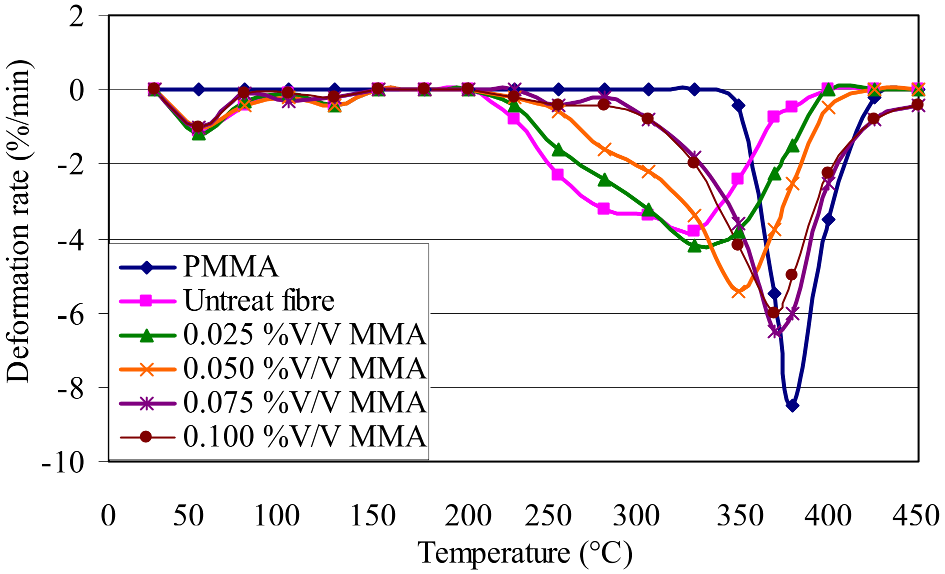


Figure 5. Deformation rate by TGA of untreated fiber, admicellar-treated fibers with various amounts of MMA and PMMA.

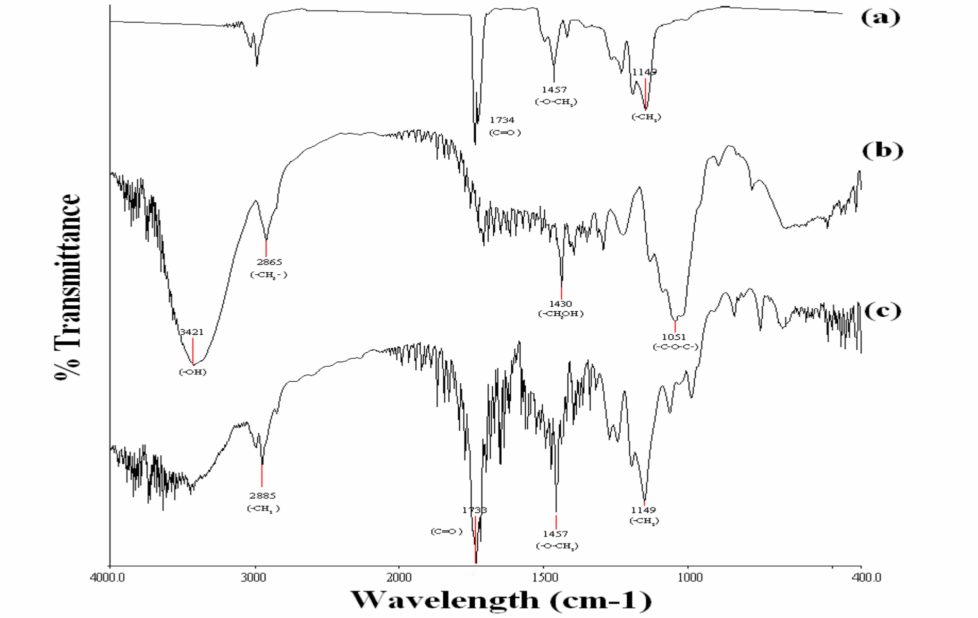
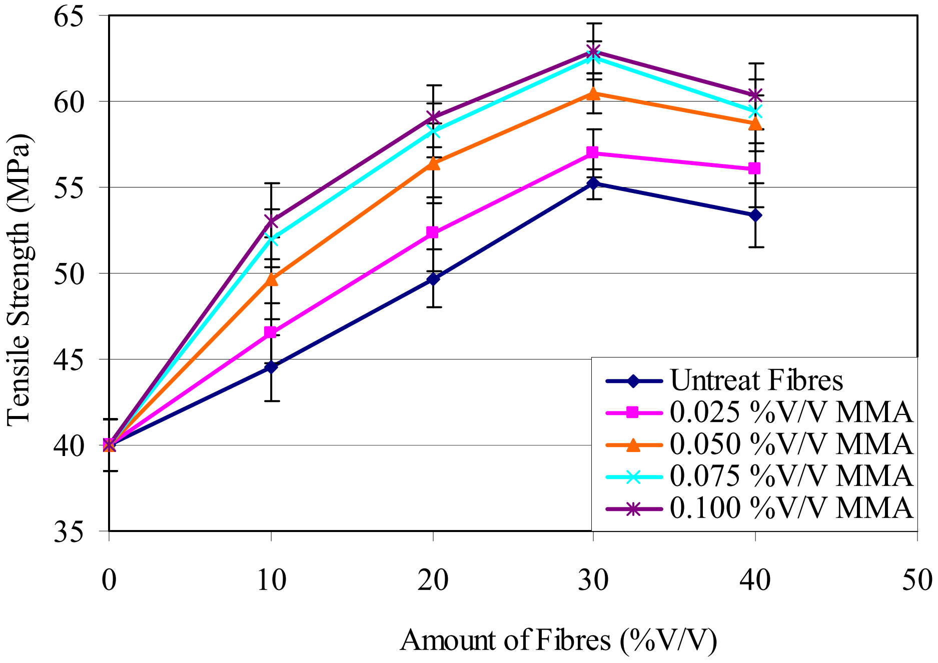
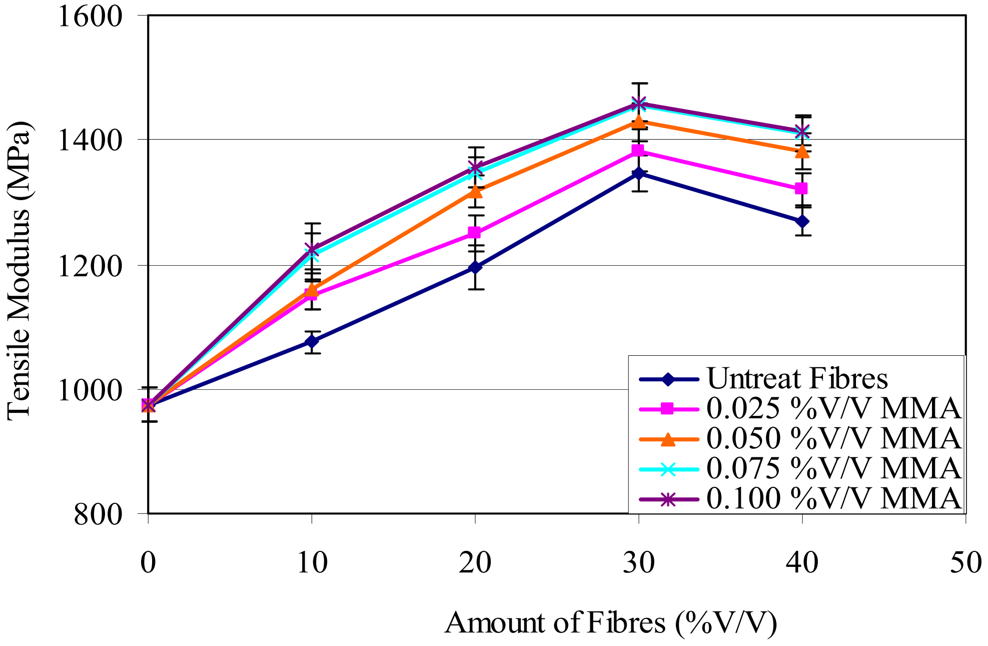


Figure 6. Characteristic peaks of; (a) PMMA, (b) untreated sisal fiber and (c) admicellar-treated sisal fiber.

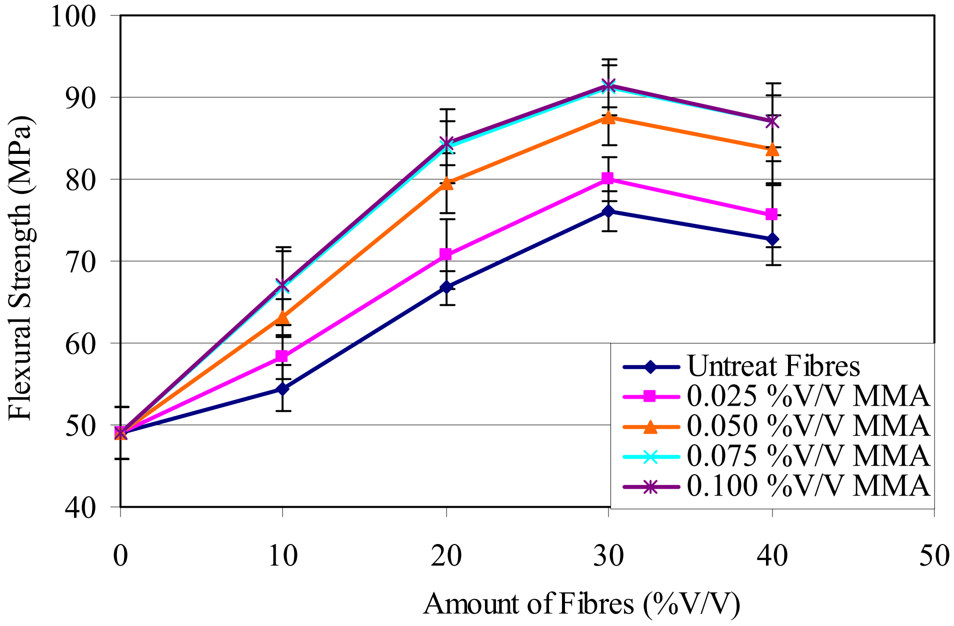


(a) Tensile Strength

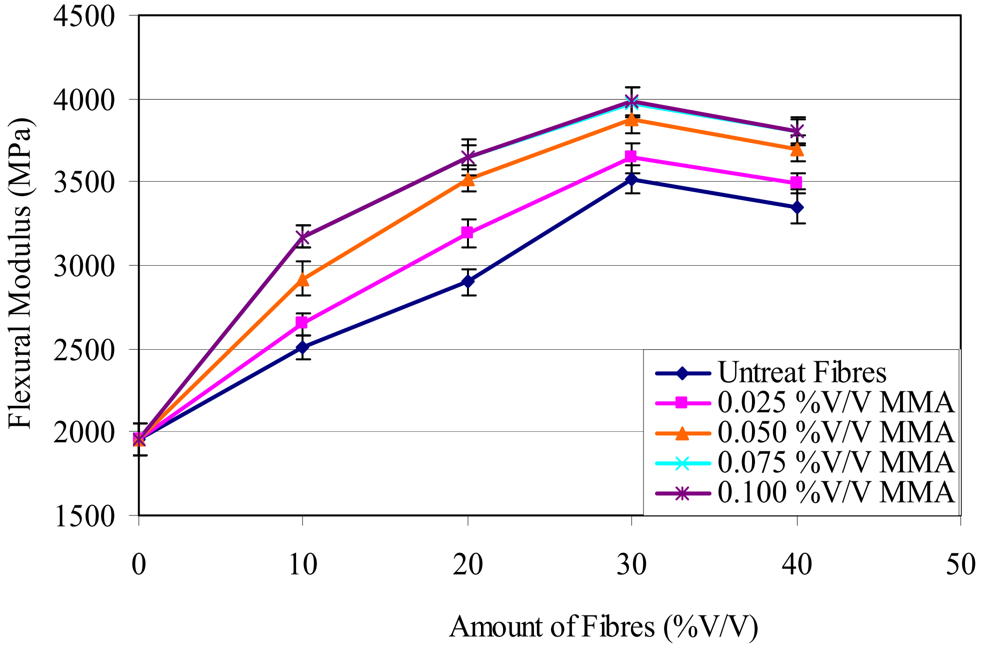


(b) Tensile Modulus

Figure 7. The effect of untreated and admicellar-treated fiber content on (a) tensile strength, and (b) tensile modulus of the composites (using 10-mm fiber length).



(a) Flexural Strength



(b) Flexural Modulus

Figure 8. The effect of untreated and admicellar-treated fiber content on (a) flexural strength, and (b) flexural modulus of the composites (using 10-mm fiber length).

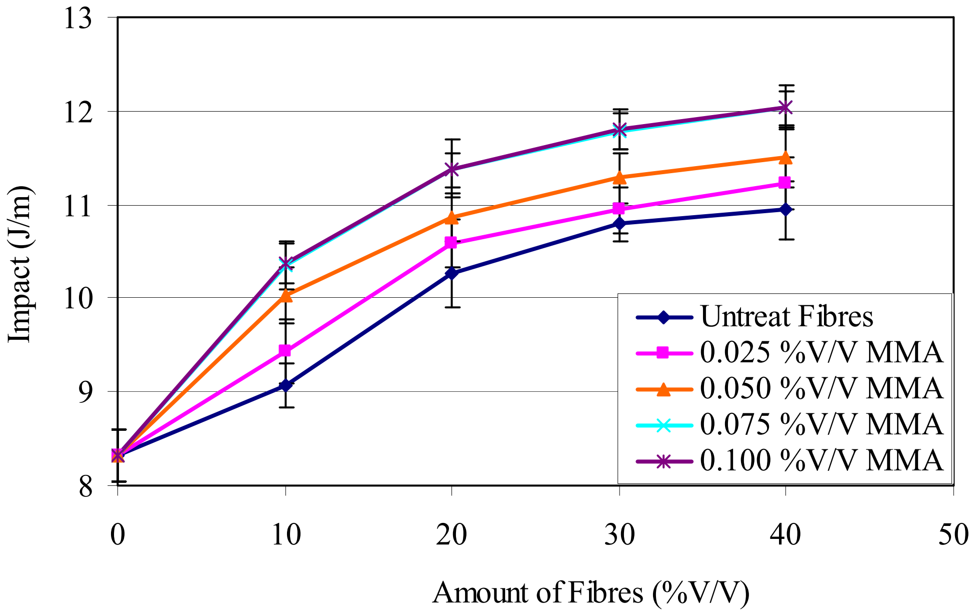


Figure 9. The effect of untreated and admicellar-treated fiber content on the impact strength of the composite (using 10-mm fiber length).

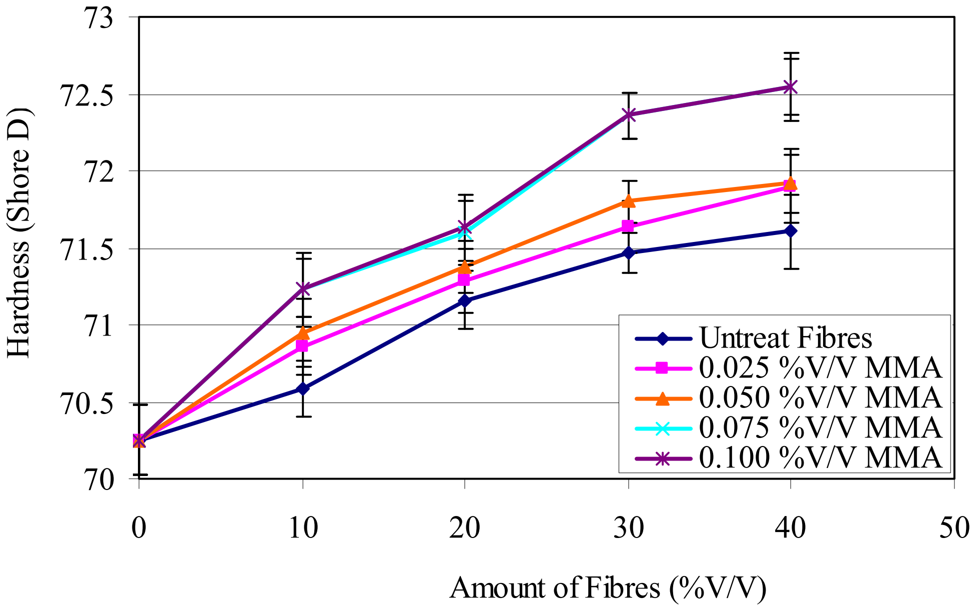
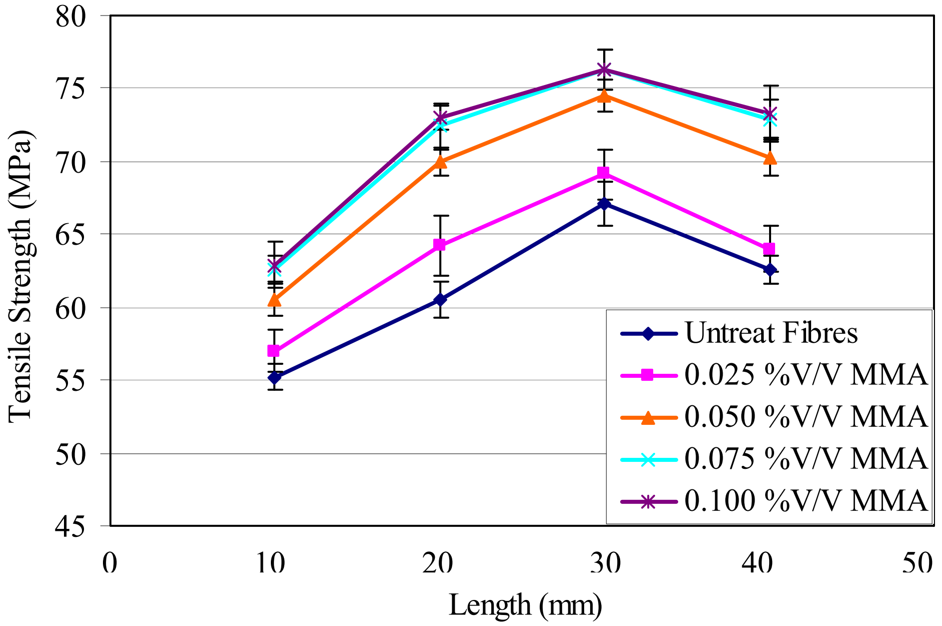
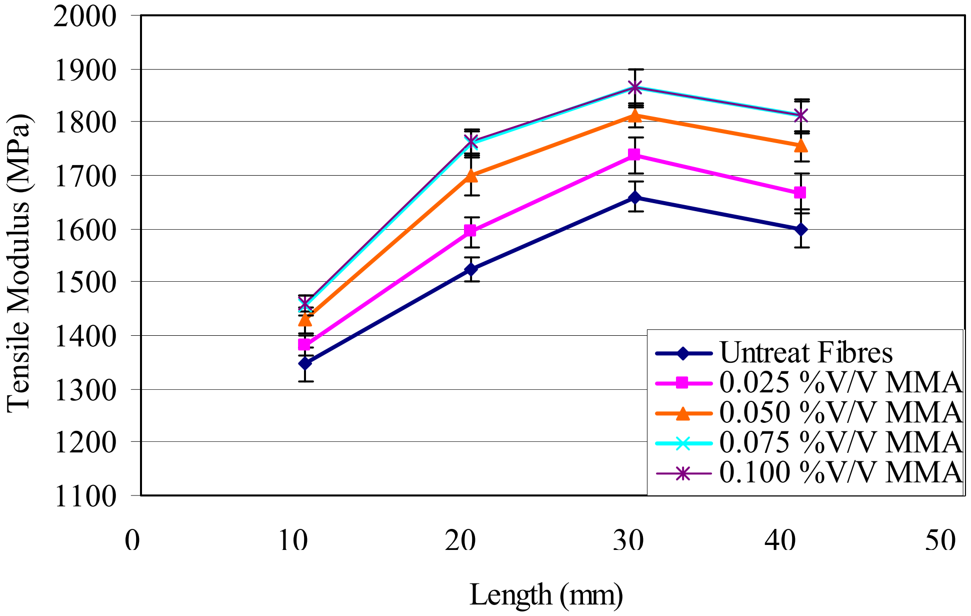


Figure 10. The effect of untreated and admicellar-treated fiber content on the hardness of the composite (using 10-mm fiber length).

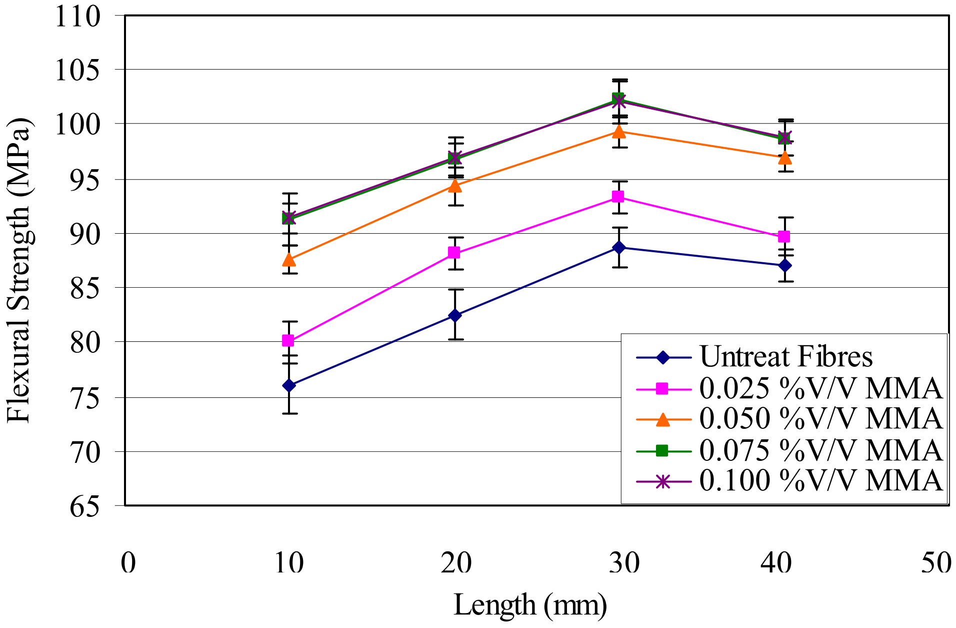


(a) Tensile Strength

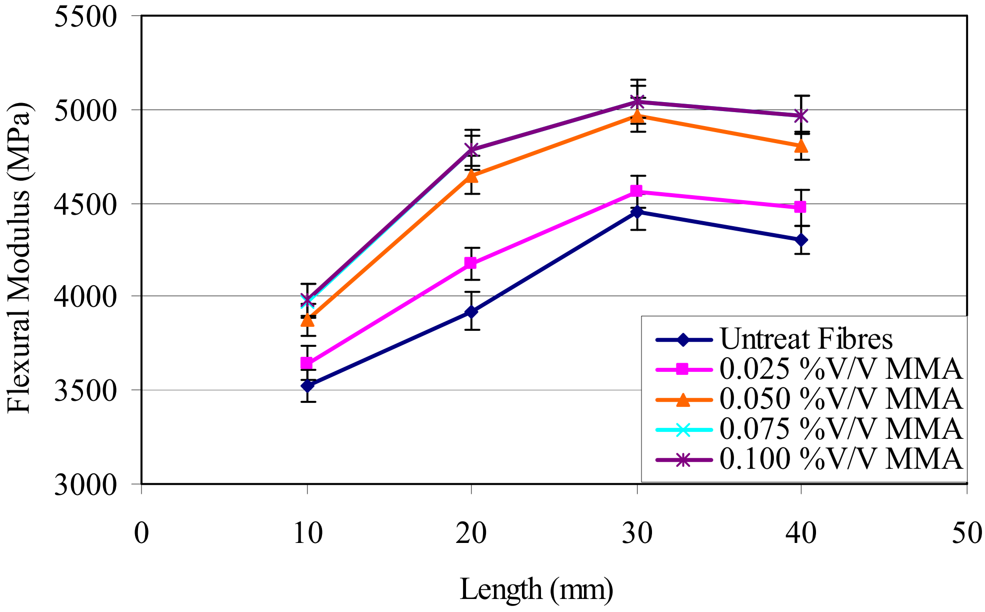


(b) Tensile Modulus

Figure 11. The effect of untreated and admicellar-treated fiber length on (a) tensile strength, and (b) tensile modulus of the composite (using 30 %V/V fiber loading).



(a) Flexural Strength



(b) Flexural Modulus

Figure 12. The effect of untreated and admicellar-treated fiber length on (a) flexural strength, and (b) flexural modulus of the composite (using 30 %V/V fiber loading).

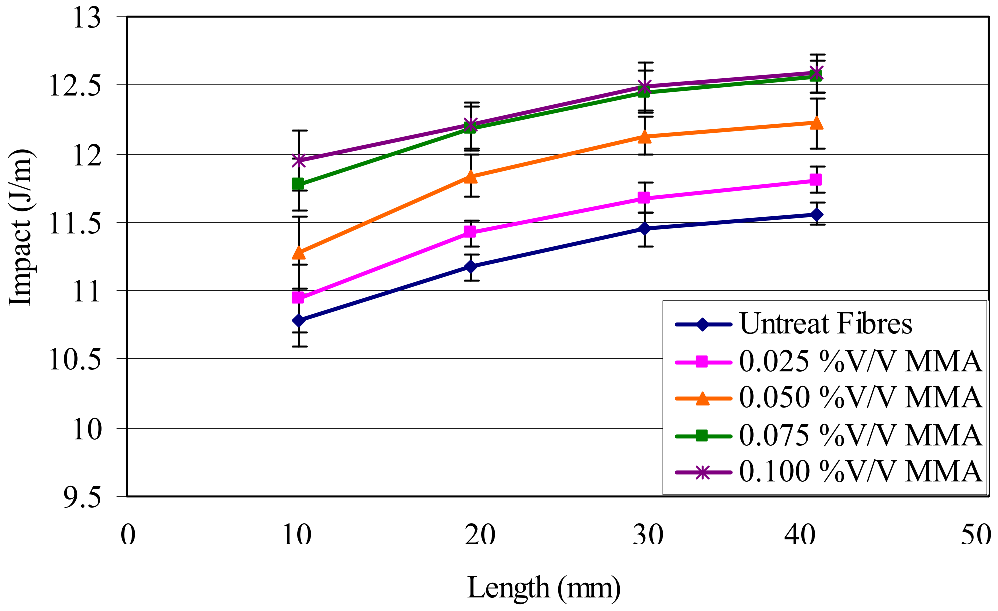


Figure 13. The effect of untreated and amicellar-treated fiber length on the impact strength of the composite (using 30 %V/V fiber loading).

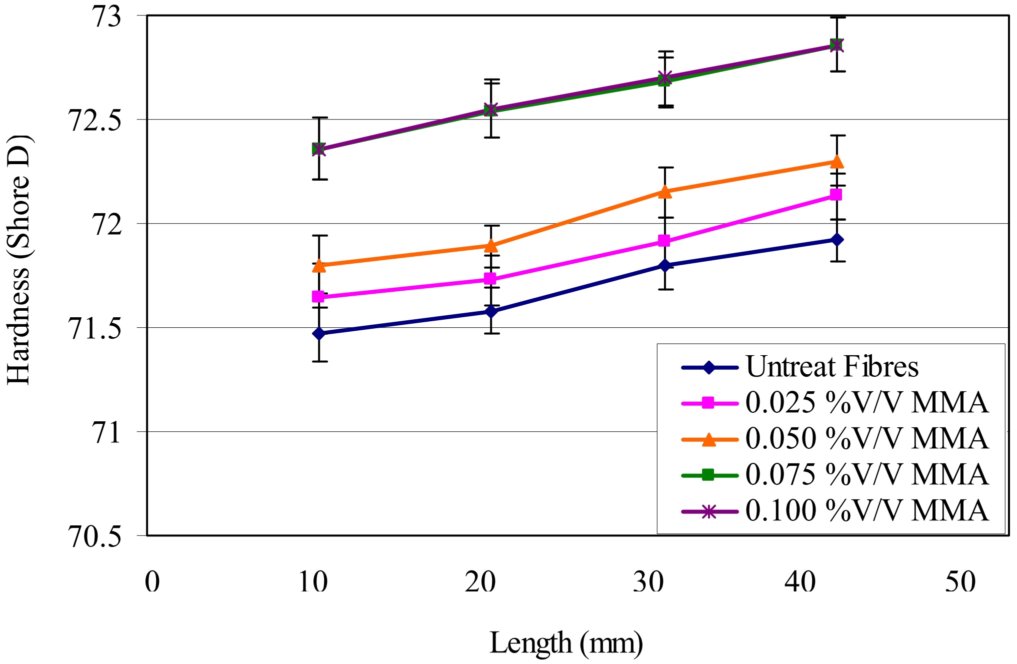
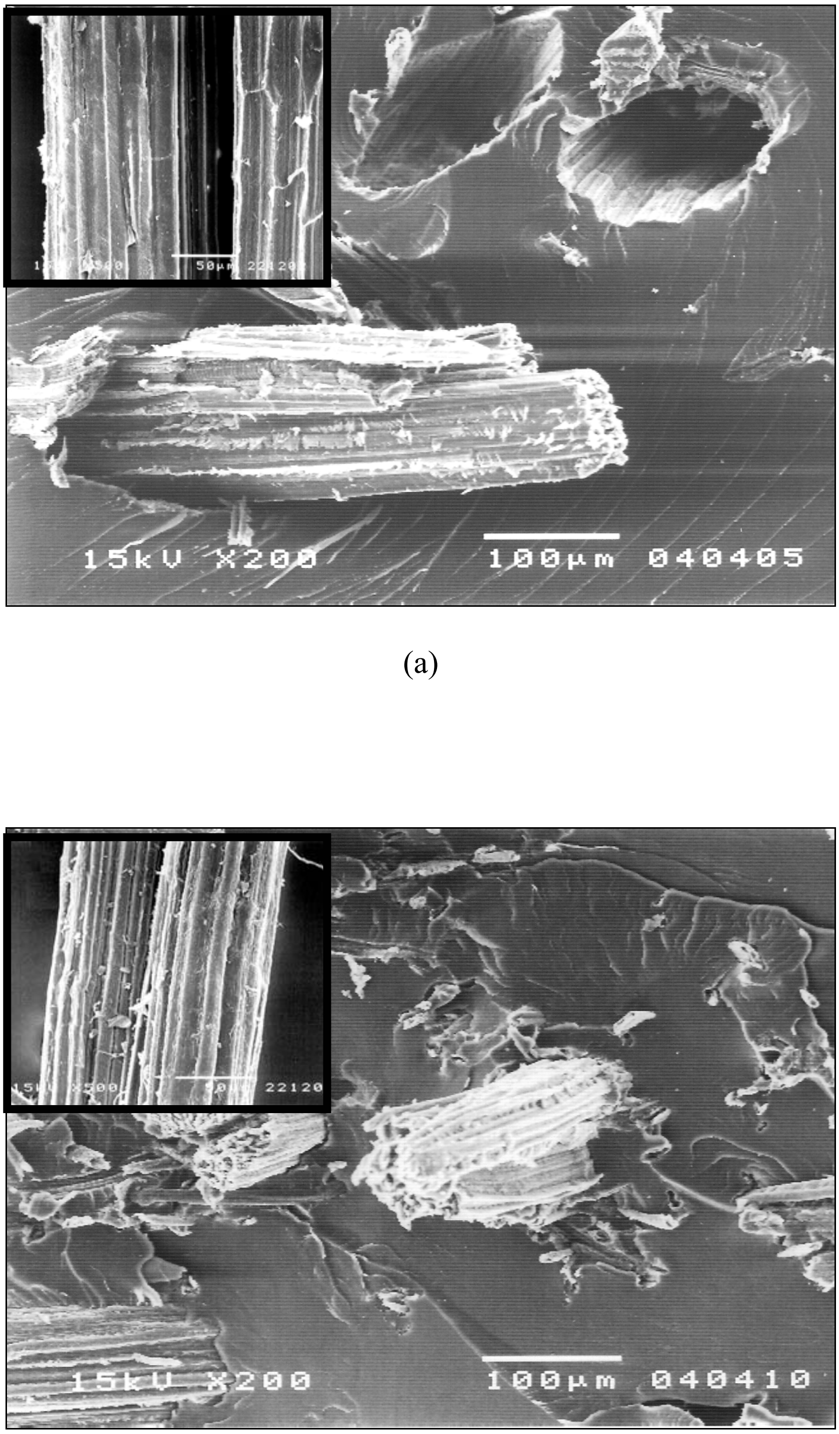


Figure 14. The effect of untreated and admicellar-treated fiber length on the hardness of the composite (using 30 %V/V fiber loading).



(a)

(b)

Figure 15. Morphology of (a) untreated and (b) admicellar-treated sisal fibers of the composite.