

Plasma-treated Abaca Fabric/Unsaturated Polyester Composite Fabricated by Vacuum-assisted Resin Transfer Molding

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To improve the adhesion and wetting between the abaca fibers and matrix, the surface of abaca fabric was modified using plasma polymerization. Different plasma exposure times were conducted to determine the effect of plasma treatment on the properties of the composites. A combination of plasma and other surface modification processes was also investigated to determine whether double treatments could further enhance the properties of these composites. Combined treatments involve plasma polymerization of the fabric after pretreatment with one of the following surface-modification reagents: a) γ -methacrylopropyltrimethylsilane, b) triethoxyvinylsilane, and c) 2%_{w/w} NaOH (aq). The abaca fabric/unsaturated polyester composites were fabricated using the vacuum-assisted resin transfer molding (VARTM) technique. SEM results showed that 10 to 20 seconds plasma treatment gave the right amount of surface roughness for maximum fiber and matrix adhesion leading to improved mechanical properties of the composites. Longer plasma treatment time and double treatment however resulted in composites with lower mechanical properties. Although the composite with alkali and plasma-treated fabric showed the lowest mechanical properties it exhibited the lowest water uptake in both distilled water and brine solution.

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1. Introduction

The high price of synthetic fibers and the demands for environment-friendly materials led to the search for new reinforcing materials that are both cheap and environment-friendly. The use of natural fiber in composites does not only help reduce dependence on non-renewable energy/material sources but also lowers pollutant and greenhouse gas emissions, enhances energy recovery, and end of life biodegradability of components. The mechanical properties of natural fiber composite can compete with that of the synthetic with better fiber treatment and appropriate processing technique.¹ The components of natural fibers include cellulose, hemicellulose, lignin, pectin, waxes and water soluble substances. They fall into three major types: bast fiber, core fiber, and leaf fiber. The percent composition depends on the fiber source. Abaca for example is composed of around 60% cellulose, 15 to 17% hemicellulose or pentosan, 7 to 9% lignin, and 3% ash.^{2,3} Knowledge of the chemical composition and surface bonding

properties of natural fibers is essential for developing natural fiber reinforced composites.⁴⁻⁶ Tropical countries like the Philippines abound with fibrous plants, some of which are agricultural crops. Abaca is in fact one of the top export earners for the country. Abaca fiber, known as Manila hemp, is extracted from the stalk of the plant *Musa textiles* Nee. Abaca is similar to banana in appearance except that the leaves are upright, pointed, narrower and more tapered than the leaves of banana. It is considered as one of the strongest natural fibers being three times stronger than sisal fibers. Abaca is also far more resistant to salt water decomposition than most of the vegetable fibers. The presence of strongly polarized hydroxyl groups in lignocellulose-derived natural fibers make them hydrophilic. These fibers, therefore, are inherently incompatible with hydrophobic thermoplastics and thermosets which are the commonly used matrices for fiber-reinforced composites. When unmodified natural fibers are used as reinforcements in such matrices, poor interfacial adhesion between polar, hydrophilic fiber and non-polar, hydrophobic matrix, and difficulties in mixing due

to poor wetting of the fiber with the matrix occur. This in turn leads to composites with weak interface. In addition, poor fiber-matrix interaction and the fiber's low resistance to moisture have unfavorable effect on the long term properties of the composite. On the other hand, good fiber-matrix interaction can substantially improve the moisture resistance of the composite.⁷ Several researchers have attempted to improve the interfacial bonding between the natural fibers and the matrix by altering the hydrophilic nature of the fibers. Several methods to achieve this include chemical treatment,⁸⁻¹⁴ acetylation of the hydroxyl group of the fibers,¹⁵ post-treating with urotropine and urea¹⁶ and the well-known process of alkali treatment.^{10,14-16} Alkali treatment has the potential of improving fiber strength by removing lignin, hemicellulose, and pectin. Chemical modification of fiber surface may activate hydroxyl groups or introduce new moieties that can react with hydroxyl groups of the matrix, elimination of weak boundary layers and improvement of the wetting between the matrix and fibers. This reduces fiber diameter resulting to an increase in aspect ratio.¹⁶ Alkali treatment also increases fiber roughness. On the other hand, plasma treatment using atmospheric glow discharge (AGD) with plasma source using high voltage radio frequency (RF) was used to effect both fiber roughness and polymerization on the fiber surface (by introducing the appropriate monomer into the chamber).

In this study, plasma polymerization and plasma polymerization in combination with other surface modification processes (pretreatment of fiber with alkali and silane coupling agents) was applied to abaca fabrics. The mechanical properties and water absorption of the surface-modified abaca fabric reinforced composites were then investigated. The interfacial adhesion between the fiber and the matrix was determined from the morphology of the fractured surface of the composites. It is also the aim of the study to determine the mechanical performance of composites fabricated by Vacuum Assisted Resin Transfer Molding (VARTM) since in our knowledge this technique has never been applied to unsaturated polyester and natural fiber.

2. Materials and Methods

2.1 Materials

The abaca fibers used in this study were selected from the variety coded as S-2 and S-3 from Bicol region of the Philippines (Fig. 1(a)). The fibers were weaved into fabrics in 0/90 orientation with 3-ply in 0 degree (welf) and 1 ply in 90 degree (warp) as shown in Fig. 1 (b)&(c). The matrix used in this study is the unsaturated polyester resin (RGP-10-103) with styrene monomer, cobalt naphthanate and methyl ethyl

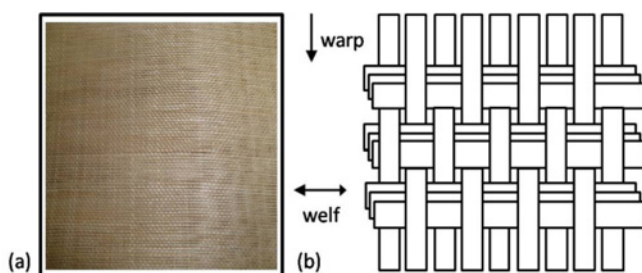


Fig. 1 Digital photo of abaca (a) fiber and (b) woven fabric, and (c) schematic representation of the weave orientation of the fabric

ketone peroxide (MEKP). All of these reagents were purchased from Polymer Products Inc, Philippines. The silane coupling agents used for surface treatment, triethoxyvinylsilane (trisilane) and γ -methacrylopropyltrimethylsilane (methasilane), were purchased from Japan. Other chemicals such as sodium hydroxide and acrylic acid were used without further purification.

2.2 Surface Modification

2.2.1 Alkali Treatment

The abaca fabric was soaked in 2% w/w NaOH (aq) solution for 30 minutes at room temperature. This condition was established after optimizing the alkali solution concentration, soaking time, and soaking condition (room temperature or boiling temperature) in the preliminary experiments. The alkali-treated fabric was then rinsed repeatedly with distilled water until the rinsing reaches pH 7 as monitored by pH meter. The alkaline treated fabric was air-dried for 2 to 3 days and stored in zip lock bags. The moisture content of the fabrics determined by digital moisture meter (Denver IR-60) was about 5-7%.

2.3 Silane Coupling Agent Treatment

Two types of silane coupling agent were used to modify the surface of abaca fabric: triethoxyvinylsilane (referred here as tri-silane) and γ -methacrylopropyltrimethylsilane (referred here as metha-silane). The abaca fabric was washed with water for several times and then dried prior to treatment. Both silane treatments follow the following steps: 1) 0.8 g silane was added to 20 mL of solution of acetone/acidified water (95:5 v/v, pH 3) to form a hydrolyzed silane solution. The solution was left for 15 minutes; 2) The pre-dried fibers were immersed in the solution, and 3) the treated fabric was air dried for 24 hours and oven dried at 60°C for 24 hours.

2.4 Plasma Polymerization Treatment

Plasma treatment was generated in glow discharge manner which was operated in closed and semi-automatic system. The sample was placed on the ground electrode in the middle of the reactor. As shown in Fig. 2, the abaca woven fabric was placed between the electrode plates where the plasma polymerization takes place. Helium was used as purging gas and as carrier gas of the acrylic acid monomer that will create a thin hydrophobic layer on the surface of the fabric during plasma-initiated polymerization.¹⁷ The frequency and voltage were 20 kHz and 3 kV, respectively. The fabric was exposed to plasma at different duration (10 seconds, 20 seconds, 30 seconds, 60 seconds, and 120 seconds). Another set of fabrics which were previously treated with 2 wt% NaOH for 30 minutes, 1% triethoxyvinylsilane, and 1% γ -

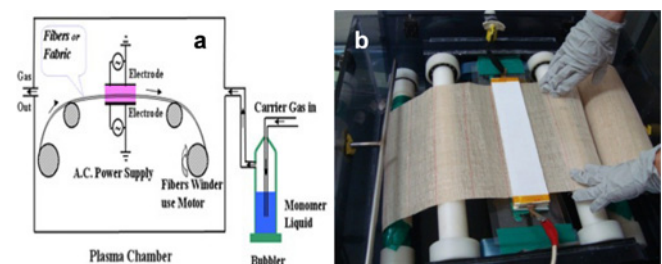


Fig. 2 Plasma polymerization set-up. (a) schematic diagram of the set-up and (b) placing the fabric inside the chamber

methacrylopropyltrimethylsilane were also subjected to plasma polymerization for 10 seconds to see whether the double treatment results to some synergistic effect on the mechanical properties of abaca fiber-reinforced composites.

2.5 Vacuum-assisted Resin Transfer Molding (VARTM)

VARTM has been used in many applications because of its capability of fabricating composites with good quality at a shorter time and at a relatively low cost. The basic steps in the VARTM fabrication process include: 1) Mold preparation and fabric lay-up; 2) Sealing the mold and creating a vacuum; 3) Preparation and degassing of the resin; 4) Resin transfer; 5) Curing of the composite.

2.6 Characterization

The morphology of the fiber was examined using a Table Top SEM (Hitachi TM 3000). The images were taken at magnification of 180x and 500x. The morphology of the composites and interfacial bonding between the fiber and the unsaturated polyester matrix was examined using a Field Emission Scanning Electron Microscope (Helios NanoLab 600i) to study the changes in the fractured surfaces of the composites. The samples were taken at magnification of 100x. The infrared spectra of raw and treated abaca were recorded on a Perkin Elmer Spectrum RX1 at a scan range of 4000-500 cm^{-1} to characterize any chemical change upon treatment of abaca with NaOH, plasma, and other surface treatments.

2.7 Mechanical Testing

The tensile tests after conditioning at 25°C were carried on universal testing machine model Instron 5882 equipped with a 5-kg load cell. The tests were performed in accordance with ASTM standards D3039. The crosshead speed used was 5 mm/min for tensile testing. For the flexural test (three-point bending), specimens with nominal dimensions of 50 mm \times 25 mm \times 2.5 mm, a span length of 90 mm and a crosshead speed of 0.7100 mm/min were used. The tests were performed in accordance with ASTM standards D790-07. The izod impact test was

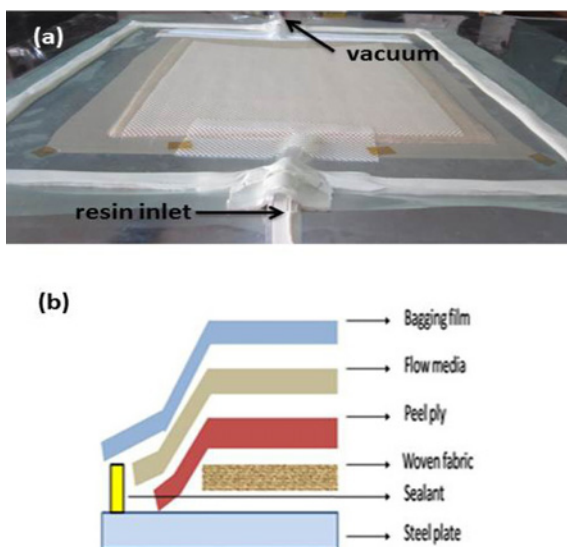


Fig. 3 Vacuum assisted resin transfer molding (VARTM). (a) actual set-up with abaca fabric, and (b) schematic representation of the different layers of the VARTM set-up

performed in accordance with ASTM D 256. The dimensions of the specimen are 63.5 mm \times 12.7 mm \times 3 mm. All the samples were cut in welf direction. The average values of the mechanical properties were obtained from 6 specimens.

2.8 Water Absorption

The dried and weighed specimens were immersed in distilled water for 24 hours and 144 hours in accordance with ASTM D5229. The specimens were cut into 25.5 \times 25.5 \times 2 mm³. Prior to absorption experiments, five specimens for each treatment were dried in an oven for 24 hours at 102 \pm 3°C. For each measurement, specimens were removed from the water and the surface water was wiped off using blotting paper. Weight change measurements were made using a micro-balance. The values of water absorption in percentage were calculated as follows:

$$WA (\%)_t = (Mc - Mo)/Mo \times 100$$

where WA (t) is the water absorption at time t, Mo is the mass of the dried specimen and Mc is the mass of the specimen as a function of immersion time.

3. Results and Discussion

3.1 Mechanical Properties

The duration of plasma treatment on the abaca fabric affects the mechanical properties of the resulting composite (Fig. 4). Plasma treatment of the abaca fabric for 10 to 20 seconds resulted to composites with the highest tensile strength while plasma treatment at an extended period tends to lower the tensile strength of the abaca-unsaturated polyester composite. The figure also shows that extending the treatment for up to two minutes diminishes the reinforcing effect of

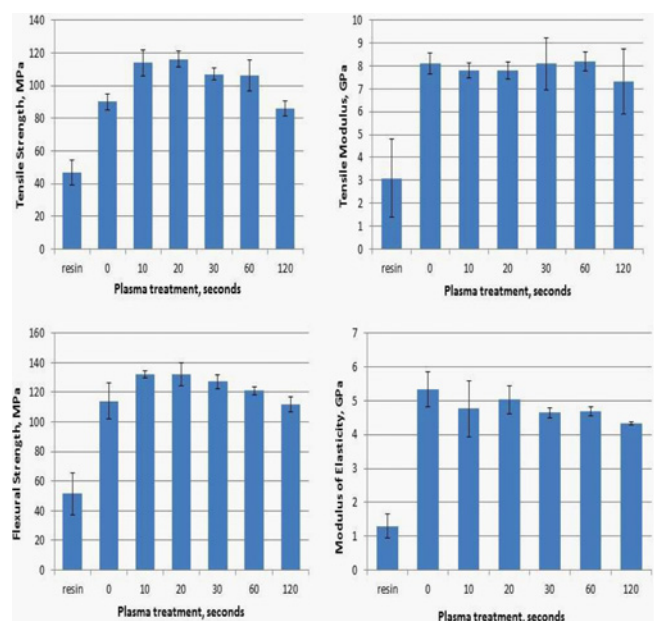


Fig. 4 Tensile and flexural properties of abaca fabric unsaturated polyester composites using abaca fabric of different plasma treatment times

plasma treatment. The unfavorable effect of extending the plasma treatment beyond twenty (20) seconds was also evident in the result of the Izod impact test of the composites (Fig. 5). Abaca fabric exposed to plasma polymerization for only 10 to 20 seconds again resulted to composites with improved impact strength while composites with abaca fabric that are plasma-treated for a longer period even performed worse than the composite with untreated fabric.

Several studies have reported improvement in the tensile strength of composites containing natural fibers modified by several surface modification techniques (e.g. alkali and various silane treatments), as shown in Table 1. In this study, plasma treatment was performed on abaca fabric pretreated with silane (methasilane and trisilane) and 2% NaOH (aq) to see if there is further improvement in the tensile strength of the composite if two surface modification processes were combined. Fig. 6 shows that coupling plasma and silane or alkali treatment did not lead to further improvement in the tensile strength of the composite. In fact, the tensile strength of the composite tends to decrease especially for the one involving abaca treated with both alkali and plasma.

The SEM image of the composite with the combined alkali and plasma treatment (Fig. 7(f)) may not provide enough information to account for its noticeably low tensile strength. One possibility is that the double treatment may have affected the integrity of the fiber itself. The Fourier Transform Infrared (FTIR) spectra and SEM images of abaca fiber that underwent similar treatments may support this claim.

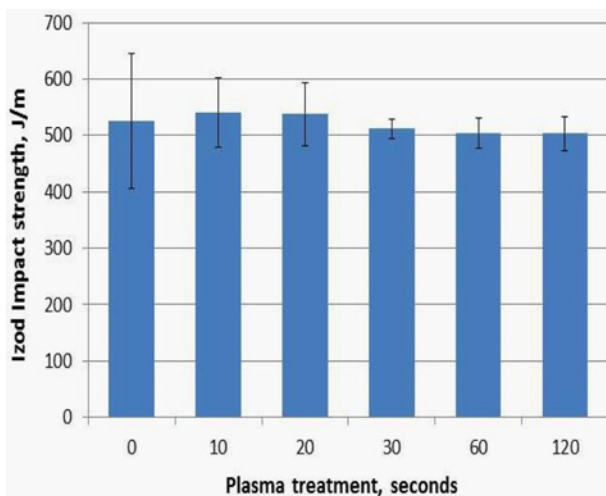


Fig. 5 Izod impact strength of abaca fabric-unsaturated polyester

Table 1 Tensile strength of composite using different surface- modified abaca fibers

Surface treatment	Tensile strength, MPa
Unsaturated polyester abaca fibers composite by Hand-lay up technique	
1% γ -methacrylopropyl trimethylsilane	49.44 (± 2.77)
1% triethoxyvinylsilane	61.79 (± 13.61)
10% Peroxide	64.79 (± 10.54)
3% NaOH	40.48 (± 12.05)
Epoxy abaca fiber composite by Vacuum Assisted Resin Transfer Molding	
2% NaOH	105.10 (± 5.84)
3% NaOH	93.92 (± 10.28)
4% NaOH	56.13 (± 7.36)

Fig. 8 shows the FTIR spectra of abaca fiber exposed to plasma and a combination of alkali and plasma treatments. Comparing the FTIR spectra of the untreated and plasma-treated fibers, it can be deduced that plasma treatment did not result to noticeable structural changes in the abaca fiber. Alkali treatment on the other hand resulted to the disappearance of the absorption band at 1732 cm^{-1} (Fig. 9, encircled). This vibration frequency is attributed to C = O group of the carbonyl or carboxyl structure.¹⁸ The disappearance of this particular band/peak in the alkali-treated fiber indicates the removal of lignin, waxes and oils on the external surface of the fibrils. It also depolymerizes cellulose

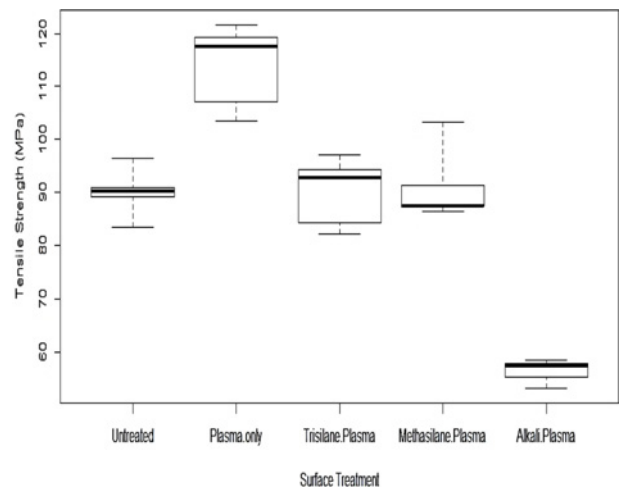


Fig. 6 Boxplot of the tensile strength of composites using various surface-modified abaca fabric

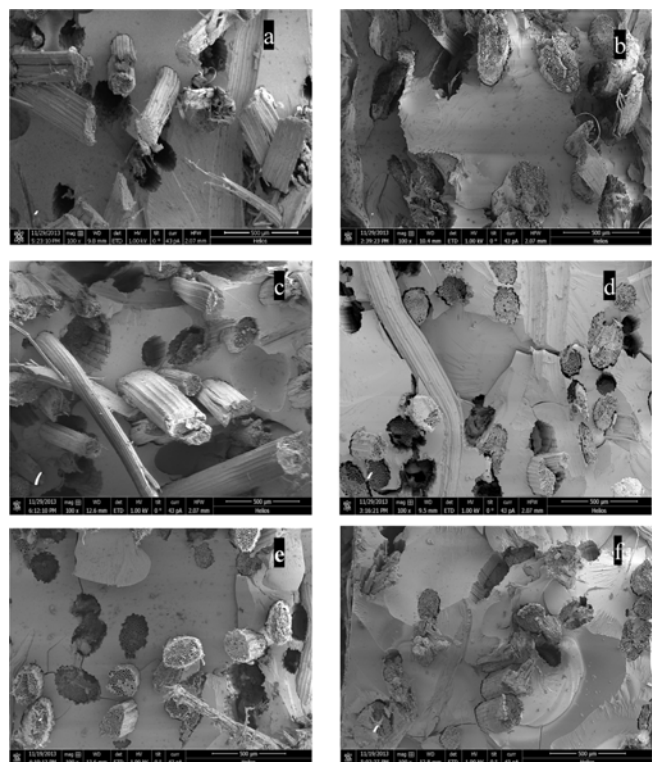


Fig. 7 SEM images of abaca fabric reinforced unsaturated polyester containing (a) untreated fiber (b) plasma treated for 10 sec (c) plasma treated for 20 sec and with pretreatment prior to plasma treatment for 10 sec (d) triethoxyvinylsilane (e) γ -methacrylopropyltrimethylsilane (f) 2% NaOH

and exposes the short length crystallites.⁴ This change in the components of the alkali-treated fiber makes it easily etched by plasma treatment. Fig. 9(d) clearly shows this effect. The combined treatment resulted to an etched surface as well as disintegration of principal strands and microcracks. This surface roughness may contribute to

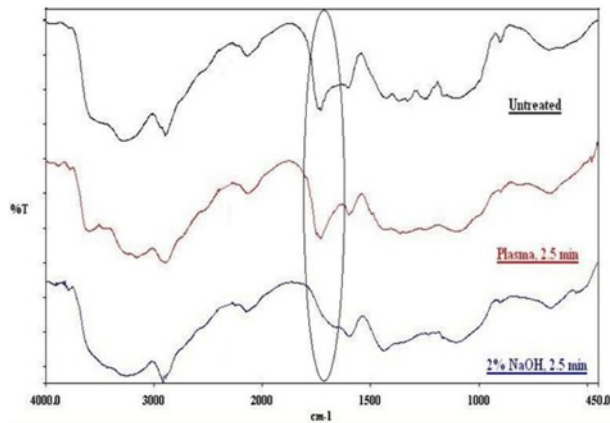


Fig. 8 FTIR spectra of abaca fiber after treatment with plasma and combined alkali and plasma treatment

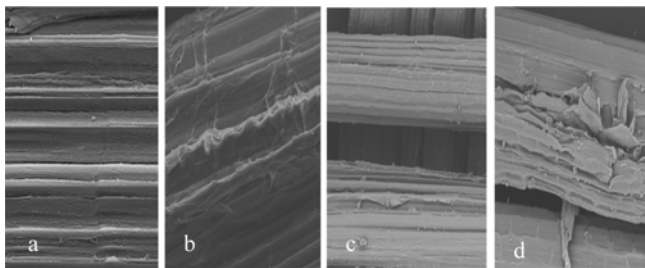


Fig. 9 Representative SEM images of (a) untreated, (b) alkali-treated (3% NaOH), (c) plasma-treated (2.5 min), and (d) 2% NaOH + plasma (2.5 min)-treated abaca fabric

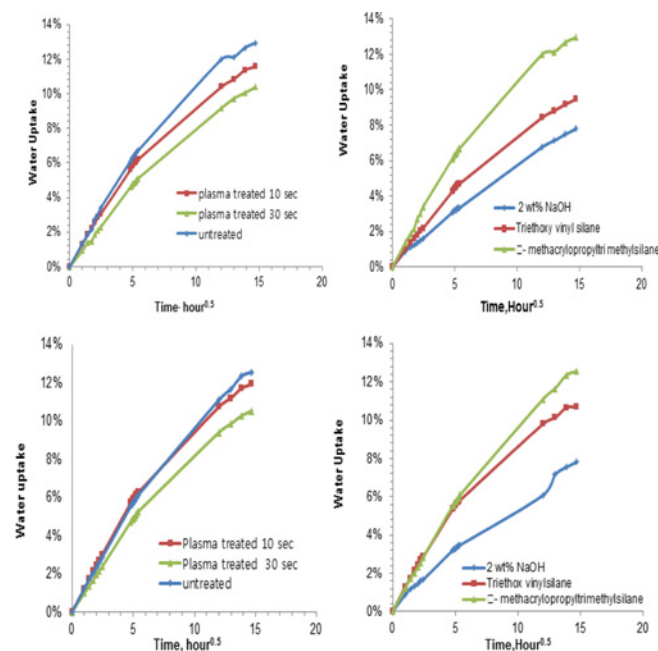


Fig. 10 Water uptake of composites (a) & (b) in distilled water (c) & (d) brine solution

increased interfacial adhesion but may have also lowered the strength of the fabric, resulting to fiber breakage and/or splitting.

3.1 Water Absorption

The water immersion test was done to evaluate the effect of plasma treatment and double treatment on the water uptake of abaca fabric reinforced unsaturated polyester composite. Fig. 10 shows the percentage of water uptake of the different composites in distilled water and brine solution as a function of square root of time. It shows that for both media, the moisture uptake increased with time indicating that the water molecules penetrate into the composites resulting to an increase in the composite weight. Initially, the weight increases abruptly due to the rapid water penetration into the composites. The figures show sharp increase and continue to increase gradually in time. In distilled water, the composite with fabric plasma treated for 30 seconds exhibited lower water uptake in two different media than the one with the fabric plasma-treated for only 10 seconds. Of the silane-plasma treated fabric/unsaturated polyester composites, the one with metha-silane has the higher water uptake than the composite with tri-silane/plasma treated fabric. This was also observed in brine solution. The combination of 2% NaOH (aq) and 10 seconds plasma treatment has the lowest water uptake both in distilled water and brine solution.

4. Conclusions

Plasma polymerization of abaca fabric leads to enhancement of adhesion and wetting of the fiber and the unsaturated polyester matrix. Effective plasma treatment must be limited to 10 to 20 seconds to achieve maximum improvement in the tensile properties of the composite. Combining plasma treatment and other surface modification processes such as γ -methacrylopropyltrimethylsilane (methasilane), triethoxyvinylsilane (trisilane), and 2%_{w/w} NaOH (aq), does not further improve the tensile properties of the abaca-unsaturated polyester composite. The composite made from abaca fabric treated with both alkali and plasma treatment in fact showed a noticeably low tensile strength. However, despite its low tensile strength, it exhibited the lowest water uptake in both distilled water and brine solution. The poor mechanical performance of the composites maybe attributed to volatilization during curing of unsaturated polyester which led to the formation of voids.

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