# THE EFFECT OF CHEMICAL TREATMENT METHODS ON THE OUTDOOR PERFORMANCE OF THE WASTE TEXTILE FIBER REINFORCED POLYMER (T-FRP) COMPOSITES

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## ABSTRACT

In this study, weathering effect on untreated Textile Fiber Reinforced Polymer (T-FRP) composites and the effect of different chemical treatments for better interfacial adhesion on the outdoor performance were investigated. Degradation of physical, mechanical and chemical properties of T-FRP composites was evaluated through common chemical treatments such as maleated coupling, alkaline treatment, silane treatment and alkali-silane treatment. Chemically untreated and treated T-FRP composites were subjected to water uptake and UV exposure up to 1000 hours. Tensile and impact properties were mechanically examined, and the changes on the physical properties due to water uptake, swelling and color change were investigated. In addition, Fourier Transform Infrared Spectrum (FTIR) analysis was performed in order to evaluate the chemical changes after exposure.

**Keywords** : Chemical treatments, waste textile fabrics, composite materials, weathering

## 1.INTRODUCTION

In the recent years, natural fiber reinforced composites expanded their daily use thanks to low weight, corrosion resistance and low costs. Therefore, composites with natural fibers are taking the place of those with inorganic fibers such as glass or carbon. Even though there are various natural fibers such as hemp, sisal, and wood as reinforcements in the composite industry, cotton fiber is one of the most promising natural fibers, and can be turned into fiber using waste textile fabrics [1]. According to the US Environmental Protection Agency (EPA) in 2012, textile waste occupies nearly 5% of all landfill space. Additionally, the textile recycling industry recycles approximately 1.71 million tonnes of post-consumer textile waste (PCTW) every year, which only accounts for approximately 15% of all PCTW, leaving 85% in landfills [2]. Utilizing waste textile fabrics as a filler and/or a reinforcement element in the composites is one of the efficient methods that recycle large volumes of textile waste.

Due to its hydrophilic nature, natural fibers are not compatible with hydrophobic polymers that mechanically degrade natural fiber reinforced composites. In order to increase the compatibility between fiber and polymer matrices, some techniques such as fiber surface modification, matrix modification and compabilitizers should be applied during the manufacturing process. Silane treatment is one of the most important treatments used for natural fiber modification. Silane coupling agents have alkoxysilane groups capable of reacting with the OH-rich surface at one end and a large number of functional groups at the other. These functional groups ensure a good compatibility between the polymer matrix and the fiber surface. Different studies prove the effectiveness of using the silane coupling in manufacturing of composites [3-7]. Xu et al. investigated the silane treatment on the

kenaf/polyester composites, and found that using a silane coupling agent for the modification of kenaf fiber surface promotes higher storage modulus and greater interfacial adhesion between the fiber and the matrix [3]. In another study conducted by Ismail et al, the mechanical properties were evaluated for the oil palm empty fruit bunch and the coir fiber reinforced polyester. They observed that the tensile strength, tensile modulus, tear strength, fatigue life and hardness were enhanced as a result of silane treatments [6,7].

Alkaline treatment of natural fibers is one of the largest areas of current research on composites: Alkali sensitive hydroxyl (OH) groups are broken down, which then react with water molecules (HAOH) and move out from the fiber structure. The remaining molecules create fiber–cell–O–Na groups between the cellulose molecular chains, removing certain portion of hemicelluloses, lignin, pectin, wax and oil covering fibers that hinder the interfacial adhesion between the fiber and the matrix. Natural fibers such as sisal [8], jute [9], ramie [10] and coir [11] were alkalized prior to manufacturing and the mechanical properties increased with the optimum alkalization parameters.

The addition of maleic anhydride (MA) to produce chemical bonding between natural fibers and thermoplastics is a common and well established technique, and it has proved to be effective in improving the mechanical properties of natural fiber composites by many studies [12-17]. Mohanty et al. showed an increase of 72.3% in flexural strength of jute-enforced polymer composites when treated with maleic anhydride polypropylene (MAPP). [12]. In another study, Mishra et al. [13] reported that maleic anhydride treatment reduced water absorption and improved mechanical properties in abaca, hemp and sisal fiber-reinforced novolac composites.

Natural fiber reinforced composites are more sensible to environmental degradation compared to composites with synthetic fibers due to structural differences: For example, hemicellulose is responsible for thermal degradation and moisture absorption while lignin is sensible to the UV degradation [18]. The use of such materials in outdoor applications has elicited concern about the durability of these products in outdoor environments. Therefore, UV durability and water absorption are particular concerns. It has been investigated that natural fiber reinforced composites exposed to weathering experience color change, mechanical degradation, and physical and chemical changes [ 19-23].

Even though there are various studies on the effect of weathering on natural fiber reinforced composites, studies on the effects of chemical treatments on the performance of composites outdoors, specifically T-FRP, are very limited. Considering that the use of natural fibers in composites is not possible without any chemical treatment, the specific objectives of this work are ultimately to

- Investigate the outdoor performance regarding UV exposure and water absorption of the untreated waste textile fabric polymer (T-FRP) composite.
- Investigate the effect of chemical treatments on the outdoor performance of T-FRP composites.

## 2.MATERIALS &METHODS

### 2.1 Material & Sample Preparation

Untreated composites and composites with different chemical treatments were manufactured with 25 wt% waste cotton fabrics. Chopped waste fabrics are rib-knitted; 30 Ne yarn and 100% cotton were supplied by Linens Marketing Inc., Turkey. Matrix material of the composite is low-density polyethylene (LDPE), supplied from Petkim Inc., Turkey.

In order to manufacture the composite plates, a custom-made single screw extruder was used. At the end of the extruder, a special die was used to manufacture composites in the 6 mm thick plate form. Reprocessing was performed three times to turn the waste cotton fabrics into cotton fibers and to provide better fiber homogeneity [1]. Fabrication and reprocessing sequences were shown in Figure 1. As seen in the flow chart, after the manufacturing process, composite plates were pressed to maintain constant thickness and flatness. Samples for tensile and impact testing were cut out of from the calibrated plates by using a desktop CNC milling machine.
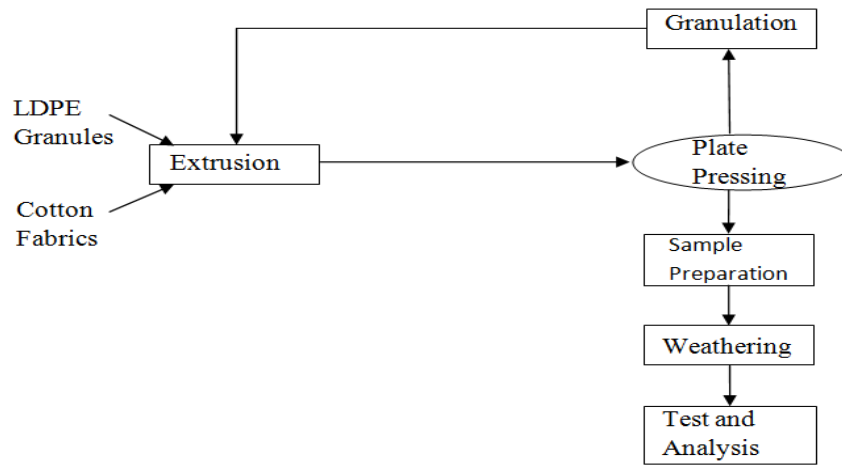
**Figure 1.** Basic composite fabrication and flow chart of the study

## 2.2 Chemical Treatments

The best parameters for the mechanical properties of T-FRP were investigated in the previous studies and chosen for each treatment in this study. For the alkaline treatment, waste cotton fabrics were immersed in the 1M sodium hydroxide (NaOH) solution for 5 hours at room temperature. After immersion, they were washed in distilled water until a pH of 7 in rinsed solution was obtained. Finally, the fabrics were dried in an oven at 60°C for a period of 6 hours before manufacturing. Sodium hydroxide (NaOH) was supplied from Merck & Co., Inc (USA). 1.5 % by weight of (3-Mercaptopropyl) trimethoxysilane supplied from Sigma-Aldrich Chemicals (USA) was diluted in a 50% aqueous solution of methanol for silane treatment. The pH of the solution was maintained between 4 and 5 using acetic acid. The fabrics were immersed in the solution for 3 hours at room temperature before being washed with distilled water. Finally, the fabrics were dried in the oven at 60°C for a period of 6 hours. For alkali - silane treatment, alkaline treatment was applied to the fabrics followed by the silane treatment with the best parameters mentioned before. FusaBond E226 supplied from

DuPont (USA) as a coupling agent in the ratio of 5 wt% was used for the maleic anhydride coupling.

In the table 1 the materials used for this study is seen with designations and short explanations.

**Table 1.** Designations and material contents used in the study

| Designation | Chemical Treatment | Explanation |
|---|---|---|
| **LDPE** | - | Pure low density polyethylene |
| **T-FRP** | - | Composite without treatment (includes 25 wt% cotton fiber) |
| **+Si** | Silane | T-FRP +1.5 wt% Silane (3h) |
| **+NaOH** | Alkaline | T-FRP+ 1 M NaOH (5h) |
| **+NaOH-Si** | Alkali - silane | T-FRP+ 1 M NaOH (5h) + 1.5 wt% Silane (3h) |
| **+MA** | Maleic anhydride coupling | T-FRP+ 5 wt% Maleic Anhydride |

## 2.3 Weathering, test and characterization

### 2.3.1 UV exposure

Composite materials were exposed to both Ultraviolet (UV) light exposure and water absorption for the time periods of up to 1000 hours. The artificial UV light exposure was conducted in the UV Atlas 2000 weathering chamber with respect to ASTM G113 at constant relative humidity and temperature (50°C) with a wavelength of 300 nm.

### 2.3.2 Water Absorption

Moisture exposure studies were conducted due to ASTM D-570 test standards. The specimens were dried in an oven at 60°C for 3 hours and were allowed to cool down to room temperature. Immediately upon cooling, the specimens were weighed ($W_d$ = dry weight) and the thickness of the samples were measured. The specimens were then immersed in the distilled water bath at 25°C for different time durations. The specimens were weighed ($W_i$ = weight of moist material at a specific time) and the dimensions were measured immediately at 100, 250, 500 and 1000 hour immersion time by removing all surface water with a clean dry cloth. The moisture absorption (M = percentage weight gain) was calculated by the formula (1) :

$$M (\%) = \frac{W_i - W_d}{W_d} \times 100 \tag{1}$$

While the thickness swelling for the composites were calculated according to the formula (2) :

$$TS (\%) = \frac{T_i - T_d}{T_d} \times 100 \tag{2}$$

where TS is the thickness swelling; $T_i$ is the thickness of sample before immersion; $T_d$ is the thickness of sample after immersion.

If the content of water remained invariable in the test samples, they were removed and the tensile and impact tests were performed in order to investigate the mechanical properties.

### 2.3.3 Tensile testing

Tensile testing was performed according to ASTM D638–08: Standard Test Method for Tensile Properties of Plastics. Static tensile tests were conducted in the laboratory where the temperature was at 23 ˚C and had 50 % relative humidity. The specimens were tested using a Shimadzu AG-IS tensile testing machine fitted 50 kN load cell operated at a cross – head speed of 50 mm/min. Optical extensometers followed by two digital cameras were used to measure strains.

### 2.3.4 Impact testing

Impact testing was carried out according to EN ISO 179: 1997 and the specimens had the "type A" single notch. Test specimens were tested by using Devotrans Charpy impact testing device with the pendulum having a velocity of 3.8 m/s at room temperature.

### 2.3.5 Fourier Transform Infrared Spectroscopy *(FTIR)*

The surface chemistries of composites were evaluated using a Thermo Scientific Nicolet IS 10 FT-IR spectroscopy. Attenuated total reflectance method was used to collect IR spectra. All data was recorded at room temperature in the spectral range $450 - 4000$ cm$^{-1}$ with a signal resolution of 4 cm$^{-1}$. For pure LDPE matrix and composite materials, carbonyl index was calculated with Eq. (3) for composites and pure LDPE matrix over UV exposure time.

$$\text{Carbonyl Index} = \frac{I_{1712}}{I_{2915}} \tag{3}$$

### 2.3.6 Color Measurements

Color measurements were performed in accordance with ASTM 2244 using a Data Color 3890 spectrophotometer for the color L*a*b* coordinates. L* represents the lightness coordinate and varies from 100 (white) to 0 (grey), a* represents the red (+a*) to green (−a*) coordinate, and b* represents the yellow (+b*) to blue (−b*) coordinate. At least five replicates were measured to obtain the average values of color. In order to determine the discoloration ( $\Delta$ E) of the weathered samples, the following formula (4) was used :

$$\Delta E = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \tag{4}$$

with ΔL*, Δa* and Δb* as the difference of initial and final values of L*, a* and b* for all composite materials.

### 3.RESULTS & DISCUSSION

## 3.1 The effect of UV weathering on mechanical, chemical and physical properties

### 3.1.1 Mechanical Properties

Figure 2 exhibits the results for tensile strength plotted as a function of the UV irradiation time for pure LDPE, untreated composites, and composites with different chemical treatments. In addition, the changes in mechanical properties due to irradiation time are given in Table 2. As seen in Fig. 2, tensile strength decreases while UV radiation exposure time increases for both pure LDPE and composites. For pure LDPE, reduction in tensile strength (TS) was approximately 22% after 1000 hours UV exposure. The decrease in tensile strength for pure LDPE could be attributed to chain scission and degradation of polymer molecules during UV irradiation. However, reduction about 10-15% in TS for the composite samples, which is less than the reduction in TS of pure LDPE after 1000 hours of exposure time (Table 2), was observed, most likely due to samples having a lower amount of polymer subjected to photooxidative degradation. Therefore, these results show the advantages of composites in comparison to pure LDPE when subject to UV exposure. The decrease observed in TS for composites could be attributed to the degradation of fiber and fiber/matrix interfacial adhesion, in addition to polymer degradation with UV exposure. For almost all test samples, it was observed that TS drops are very limited (~10%) up to 250 hours, start to decrease after 500 hours, and increase significantly for longer UV exposure time to 1000 hours(~15-20%).
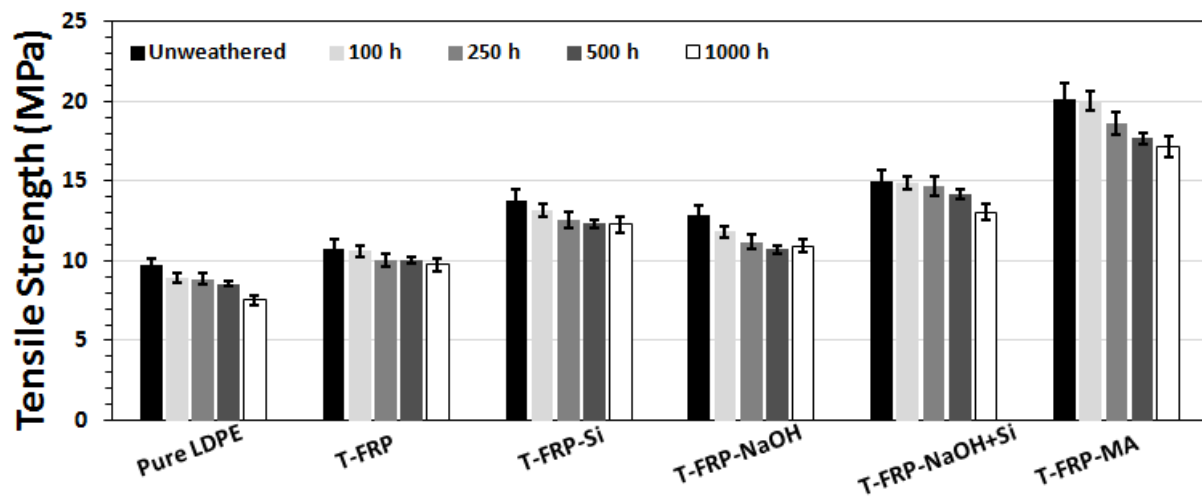


**Figure 2.** Tensile strength evolution for pure LDPE and composites with respect to UV radiation time

Another interesting observation was that the chemical methods applied for better fiber/matrix adhesion had no positive effect on tensile strength resistance for the composites during the UV exposure. Besides, the highest overall drop in TS values was observed for composites with different chemical treatments (Table 2). This is likely due to predominant degradation of fiber/matrix interfacial adhesion for the composites with treatment on the reduction of TS compared to untreated composites, which has poor fiber/matrix interfacial adhesion before weathering. Similar test results for the chemically treated composites have been reported in the study, revealing that treated composites undergo severe degradation compared to untreated composites [24]. After 1000 hours of UV radiation, drop in TS for untreated

composites was found to be around 10% while around 11-15% reduction was observed for the composites with different treatments. For various treatments, the reduction in TS varies in the order: alkaline treatment=maleic anhydride coupling>alkali – silane treated=silane treated.
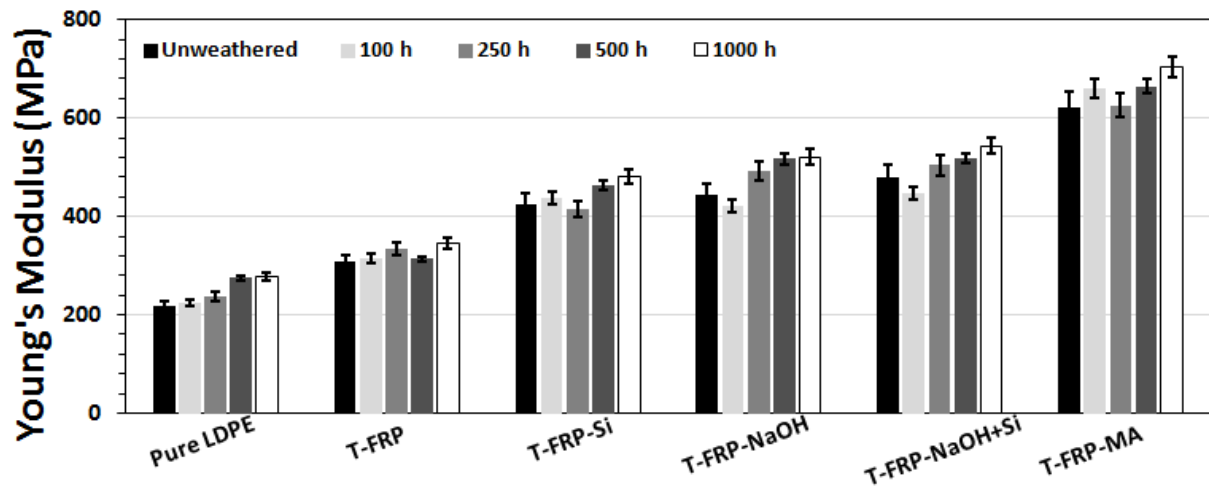


**Figure 3.** Young's modulus evolution for pure LDPE and composites with respect to UV radiation time

However, Young's modulus (YM) was found to be increased with the UV radiation time in contrast to change in TS values for all cases (Figure 3). For pure LDPE, YM remained almost constant after 250 hours of UV aging and increased gradually about 12% after 500 hours with a continued increase up 1000 hours (23%). The increase in YM for pure LDPE compared to unweathered samples might have been caused by the crosslinking of the polymer chains. Therefore, it is possible to observe the effect of crosslinking with UV aging on the YM values for all composite materials as investigated in some studies [25-29]. On the other hand, both untreated and chemically treated composites show the same trend in YM values. However, less changes in YM values after UV exposure were observed for the composites compared to pure LDPE matrix. Firstly, the composites that have less polymers are mostly affected by UV exposure; secondly, the degradation of fiber and fiber/matrix interfacial adhesion leading YM increase occurred during UV exposure. Due to the combined effect of these two mechanisms, increase in YM for the composites with UV exposure was less than the YM increase for pure LDPE. The untreated and chemically treated composites except the composite with alkaline treatment show the same stability during the weathering. The composites showed a slight increase in the first 500 hours of UV exposure, followed by an increase about 10-13% after 1000 hours of UV exposure. For the composite with alkaline treatment, YM values showed a sharp increase (16%) with 500 hours and remained constant (17%) after 1000 hours of exposure (Table 2).
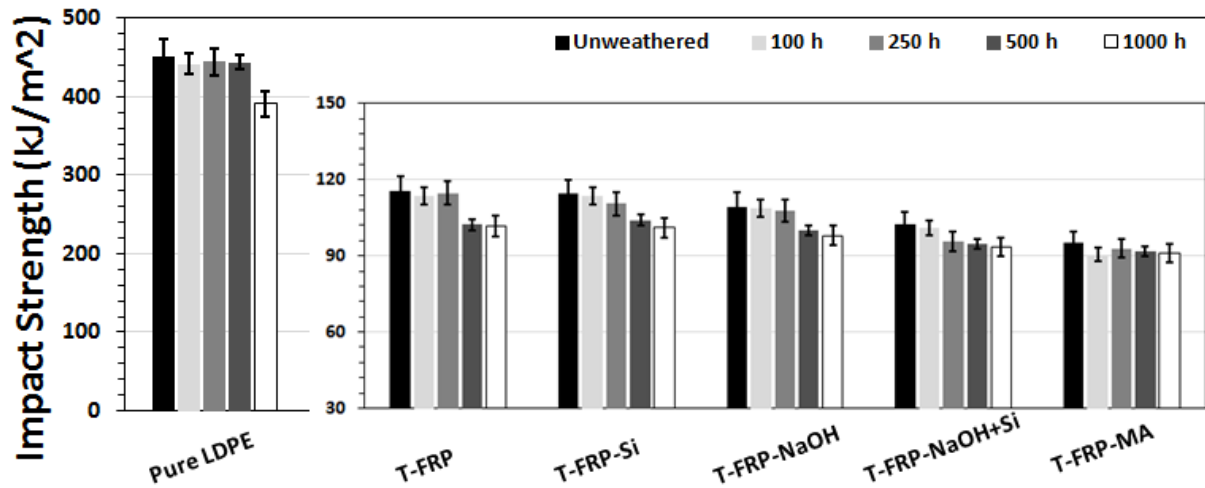
**Figure 4.** Impact strength evolution for pure LDPE and composites with respect to UV radiation time

Figure 4 illustrates the impact strength test results for both pure LDPE matrix and composites with respect to UV exposure time. As there is better adhesion and interfacial bonding between the cotton fiber and the matrix, the fiber characteristics become more dominant on the impact properties of composites according to "mixture rules". Thus, composite structures act more brittle with the cotton fibers, which are more brittle than the ductile LDPE matrix with an unweathered impact strength of 450 kJ/m$^2$ (Figure 4). This is also reported by Afrifah et al, who mentioned that the addition of natural fibers to thermoplastic matrix blocks the ductile characterization of the matrix, causing the composite structure to act more brittle [30].

**Table 2.** Change (%) of Tensile Strength (TS), Young's Modulus (YM), Impact Strength (IS) for pure LDPE and composites with respect to UV exposure time

| Change (%) | Materials | UV exposure time(h) | | | |
|---|---|---|---|---|---|
| | | 100 | 250 | 500 | 1000 |
| **TS (%)** | LDPE | -7.84 | -8.77 | -11.76 | -22.17 |
| | T-FRP | -1.86 | -6.86 | -6.90 | -9.73 |
| | T-FRP-Si | -4.65 | -8.79 | -10.45 | -10.89 |
| | T-FRP-NaOH | -7.86 | -12.99 | -16.72 | -14.86 |
| | T-FRP-NaOH+Si | -0.41 | -1.61 | -10.45 | -10.89 |
| | T-FRP-MA | -0.5 | -7.32 | -12.00 | -14.73 |
| **YM (%)** | LDPE | +2.75 | +8.92 | +26.34 | +27.61 |
| | T-FRP | +2.67 | +8.39 | +1.97 | +12.31 |
| | T-FRP-Si | +2.94 | -2.76 | +9.04 | +13.22 |
| | T-FRP-NaOH | -4.76 | +11.28 | +16.76 | +17.71 |
| | T-FRP-NaOH+Si | -6.88 | +5.02 | +8.01 | +13.07 |
| | T-FRP-MA | +5.98 | +0.73 | +6.91 | +13.32 |
| **IS(%)** | LDPE | -1.80 | -1.29 | -1.40 | -13.12 |
| | T-FRP | -1.67 | -0.96 | -11.61 | -12.16 |
| | T-FRP-Si | -0.90 | -3.44 | -8.98 | -11.69 |
| | T-FRP-NaOH | -0.50 | -1.45 | -8.66 | -10.48 |
| | T-FRP-NaOH+Si | -1.39 | -6.66 | -7.43 | -8.60 |
| | T-FRP-MA | -4.69 | -2.26 | -3.26 | -4.06 |

Overall, impact strength (IS) of the samples exposed to artificial weathering were observed to decrease as a consequence of embrittlement, surface cracks and photodegradation of polymer matrix [31]. For pure LDPE, IS was found to be stable up to 500 h. However, it was investigated to be reduced dramatically about 14% after 1000 of UV exposure (Table 2). On the other hand, IS for composites was found to be less affected than pure LDPE matrix with long exposure times. As it can be seen in table 2, it was investigated that the effect of weathering on impact strength for composites has been occured more dominantly after 250 h UV exposure following approximately 10-12% reduction was obtained with 500 h aging. In addition, it is interesting to note that chemically treated composite were found to be less affected samples compared to untreated composites. Probably, this may be likely due to the degradation of fiber / matrix adhesion that results the composite to act more ductile during UV weathering.

### 3.1.2 Chemical Properties

In order to investigate the occurence of surface oxidation of the samples, carbonyl group change was observed by FTIR spectroscopy for pure LDPE and T-FRP composites during UV weathering. Carbonyl groups are considered as the main light-absorbing species that are responsible for the degradation reactions with UV exposure in polymers.The wavenumbers of peaks used for FTIR analysis and corresponding vibrational types can be seen in Table 3. The carbonyl (CO) and hydroperoxide (OOH) frequencies are the best way to identify the effect of photo-oxidation of generated radicals.

**Table 3:** Wavenumbers of peaks used for FTIR analysis and corresponding vibrational types[*]

| Wavenumber (cm$^{-1}$) | Assignments |
|---|---|
| 3244 | O-H stretching (hydrogen bonded) |
| 2915 | C-H stretching in methyl and methylene groups |
| 1712 | C=O stretching |
| 1472 | C-H bending, crystalline |
| 1462 | C-H bending, amorphous |
| 1170 | C-O stretching |
| 730 | C-H rocking, crystalline |
| 720 | C-H rocking, amorphous |

*Sources: Ref. [33,39,40,41]

Figure 5 illustrates chemical changes for pure LDPE matrix with UV weathering. The peak around 1700 cm$^{-1}$ shows the carbonyl groups (C=O) that were formed after chain-scission or oxidation. These peaks are indicators of photo-oxidation of pure LDPE, and are also responsible for the drop in mechanical properties with UV weathering. The chain scission may be the reason behind the decrease in intensity of C-H stretching and bending vibrations near 3200 and 1470 cm$^{-1}$ respectively [32] (Figure 5). The increase in oxygen-containing functional groups is seen as a direct effect of photo-oxidation of LDPE due to UV weathering which results in the generation of polar groups such as hydroxyl, ketone, carboxyl, aldehyde, ester etc.
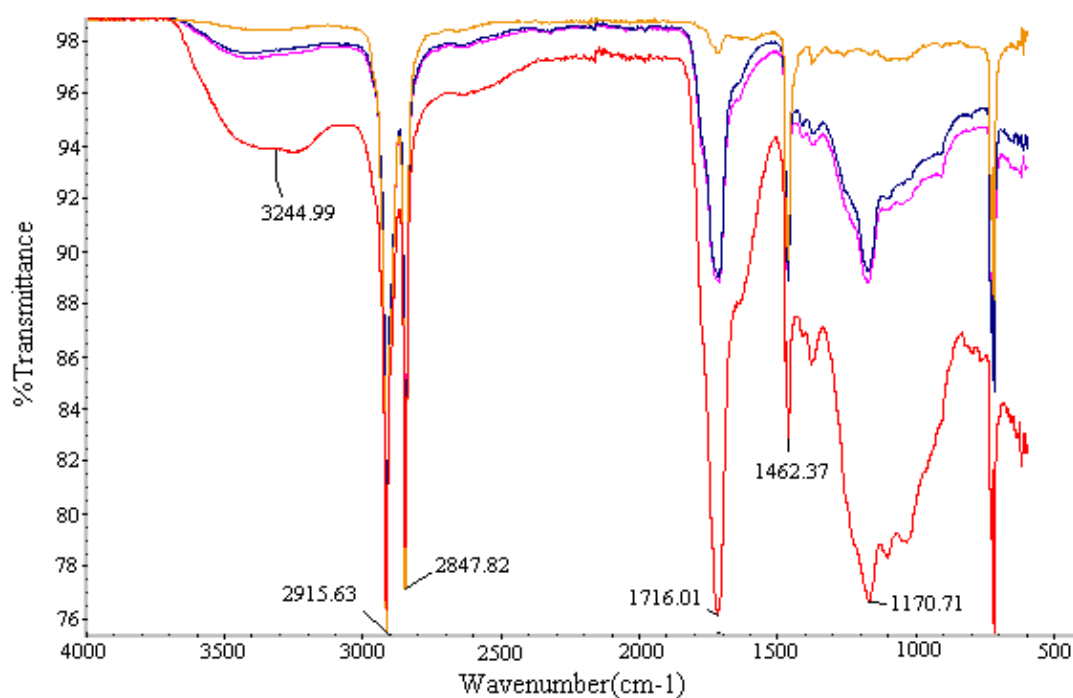


**Figure 5.** FTIR spectra of LDPE (exposition time is increasing top(0h)-down(1000h)

The absorption band intensities of 3244.99cm$^{-1}$, 1716.01cm$^{-1}$, 1170.71cm$^{-1}$ corresponding to respectively the OH groups, the carbonyl groups and bending vibrations of tertiary carbon for all T-FRP composites increased with increasing exposure time (Figures 6-8). The absorption in 1170.71cm$^{-1}$ could be due to the C-O stretching vibration and interpreted as esters, carboxylic acids and ethers which are absorbed strongly in the region 1200-1000 cm$^{-1}$ [32]. After UV weathering, the decrease in the intensities of different bands was attributed to degradation of the constituents for the T-FRP composites. All these components can undergo photo-degradation, these results are good agreement with the studies on the UV weathering of different natural fibers [33-38].
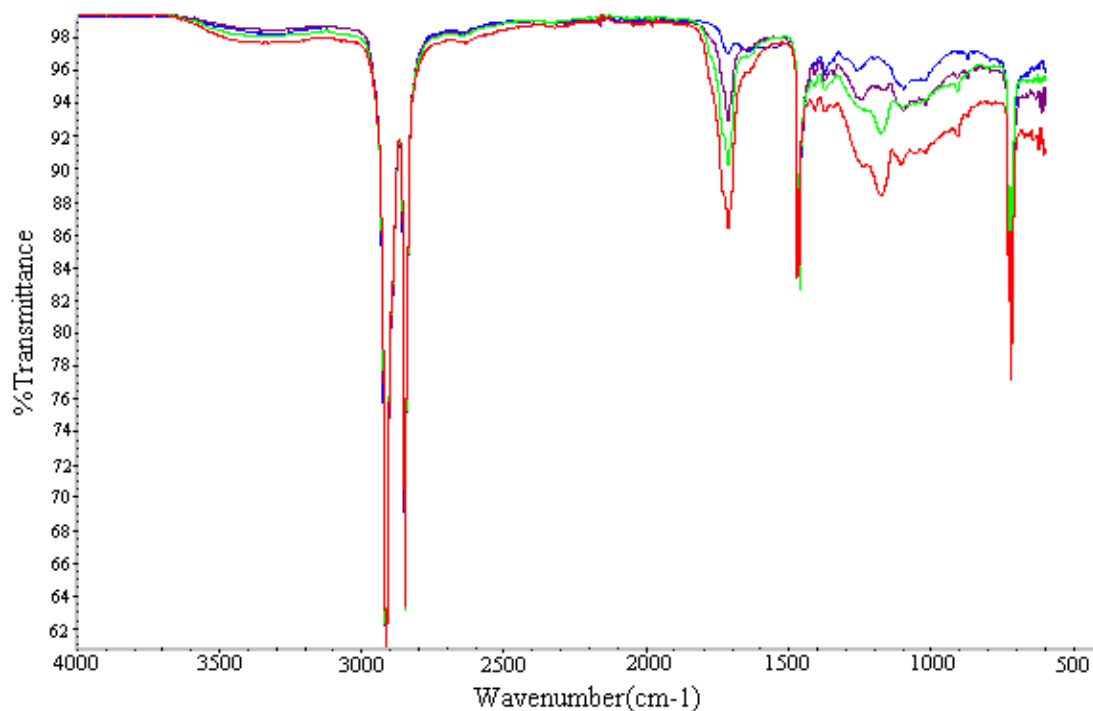


**Figure 6**. FTIR spectra of T-FRP composite (exposition time is increasing top (0h)-down(1000h)

As the UV exposure time increased up to 250 hours, infinitesimal change was observed for the carbonyl index. After 500 hours of exposure, an important discrepancy unweathered conditions was observed. This trend is well coincided with the results for mechanical properties of both the pure LDPE matrix and composites with weathering. After 1000 hours of exposure, the FTIR spectra of the T-FRP composites demonstrated that the stability of the T-FRP composites is higher than the pure LDPE. (Figures 6-8 and Table 4). However, the results show that chemically treated composites have lower stability than the untreated T-FRP composites with longer UV exposure, as chemical groups are more susceptible to oxidation for the chemically treated composites [37].
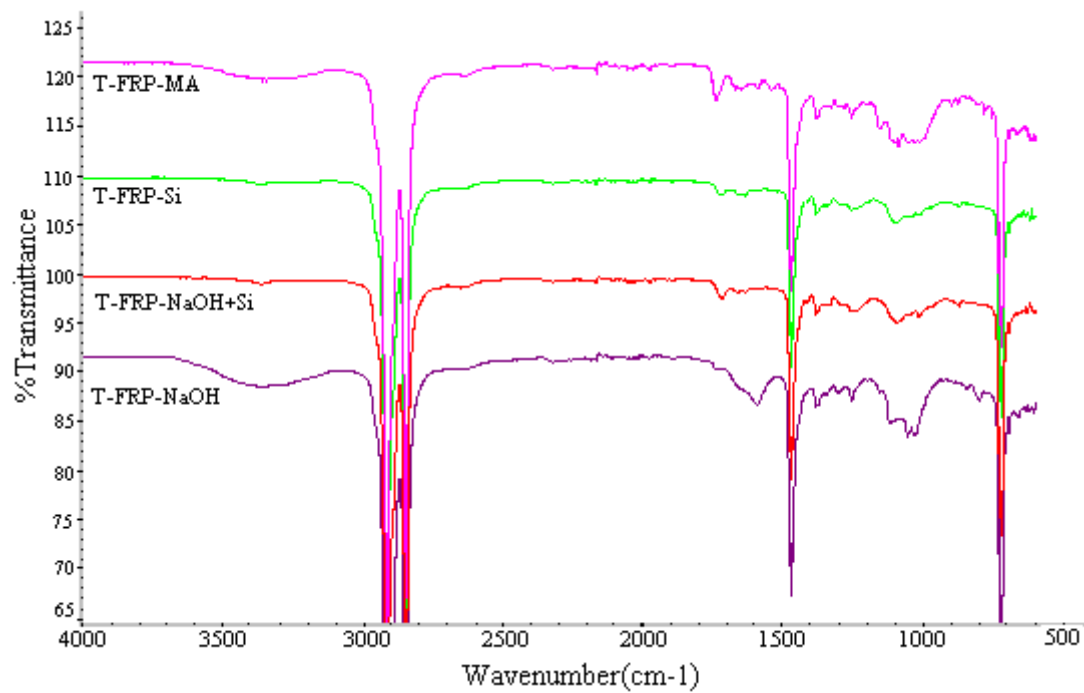
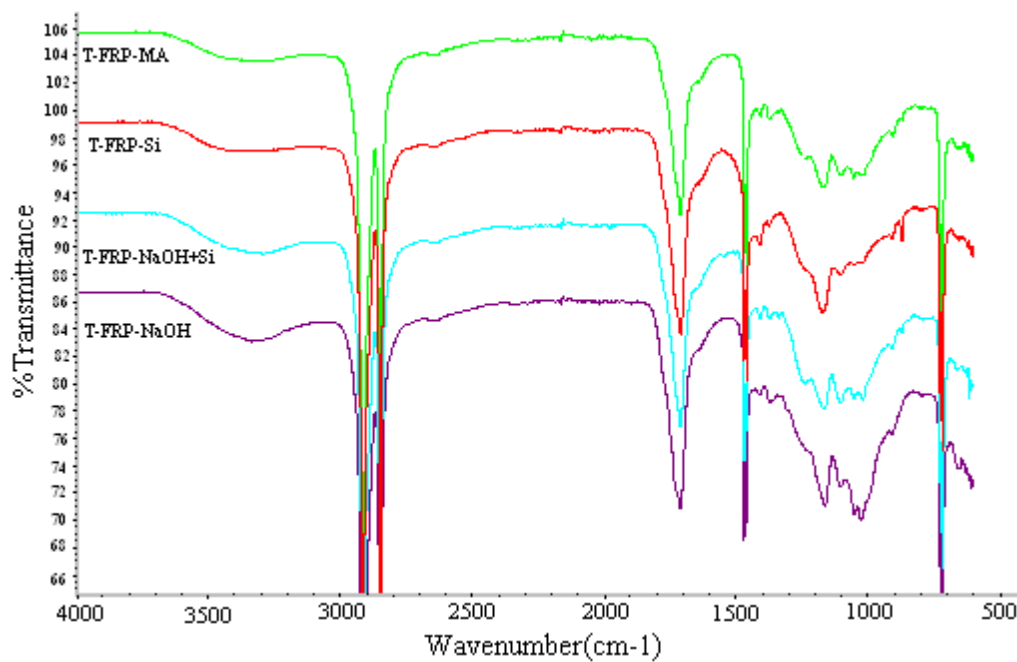**Figure 7.** FTIR spectra of treated T-FRP composites before UV weathering



**Figure 8**. FTIR spectra of treated T-FRP composites after UV weathering (1000h)

Table 4 shows the results for carbonyl index due to UV exposure time for pure LDPE and composite materials. For unweathered samples, the carbonyl index for all composite types increased compared to the pure LDPE matrix as a consequence of the cotton fiber addition, increasing the amount of oxygen and carbonyl functionality in the polymer matrix. In addition, the carbonyl index was higher for chemically treated T-FRP composites than untreated T-FRP composites. This result may have occurred because of the chemical groups in the chemical substances like silane, maleic anhydride and sodium hydroxide, which are more susceptible to undergo oxidation and decrease durability [37]. As the exposure time

increases, the carbonyl index increases at a similar rate for treated and untreated T-FRP composites and pure LDPE sample. This results confirm that the chain scission of the polymer matrix was affected by the treatment of the T-FRP composites during UV weathering.

**Table 4.** Carbonyl Index of pure LDPE and T-FRP composites

| Samples | UV Exposure Time (h) | | | | |
|---|---|---|---|---|---|
| | 0 | 100 | 250 | 500 | 1000 |
| LDPE | 0 | 0.0412 | 0.1149 | 0.28 | 0.479 |
| T-FRP | 0.0034 | 0.0262 | 0.1506 | 0.2667 | 0.346 |
| T-FRP - NaOH | 0.0065 | 0.0746 | 0.1573 | 0.2647 | 0.356 |
| T-FRP - Si | 0.0190 | 0.0436 | 0.1878 | 0.2647 | 0.3654 |
| T-FRP - NaOH+Si | 0.0264 | 0.0658 | 0.0772 | 0.2087 | 0.4033 |
| T-FRP - MA | 0.0568 | 0.092 | 0.1466 | 0.322 | 0.451 |

### 3.1.3 Physical Properties

Physical changes of composites upon UV radiation were studied by color measurements and optical microscopy observations. Figure 9 shows the changes in lightness ($\Delta L$), total color ($\Delta E$), red-green (a*) and yellow-blue (b*) of composites for different UV exposures. Visual inspections showed that the surfaces of all composites were lightened continuously with UV radiation. In some studies, it is mentioned that lignin is most susceptible to photodegradation among the constituents of lignocellulosic materials. As a consequence of photooxidation of lignin, most of the coloring substances were created by reactions between the intermediary phenoxy radicals and oxygen [42, 43]. As a good UV absorber, lignin can be responsible for the color change in the surface of cellulosic fiber reinforced composites.
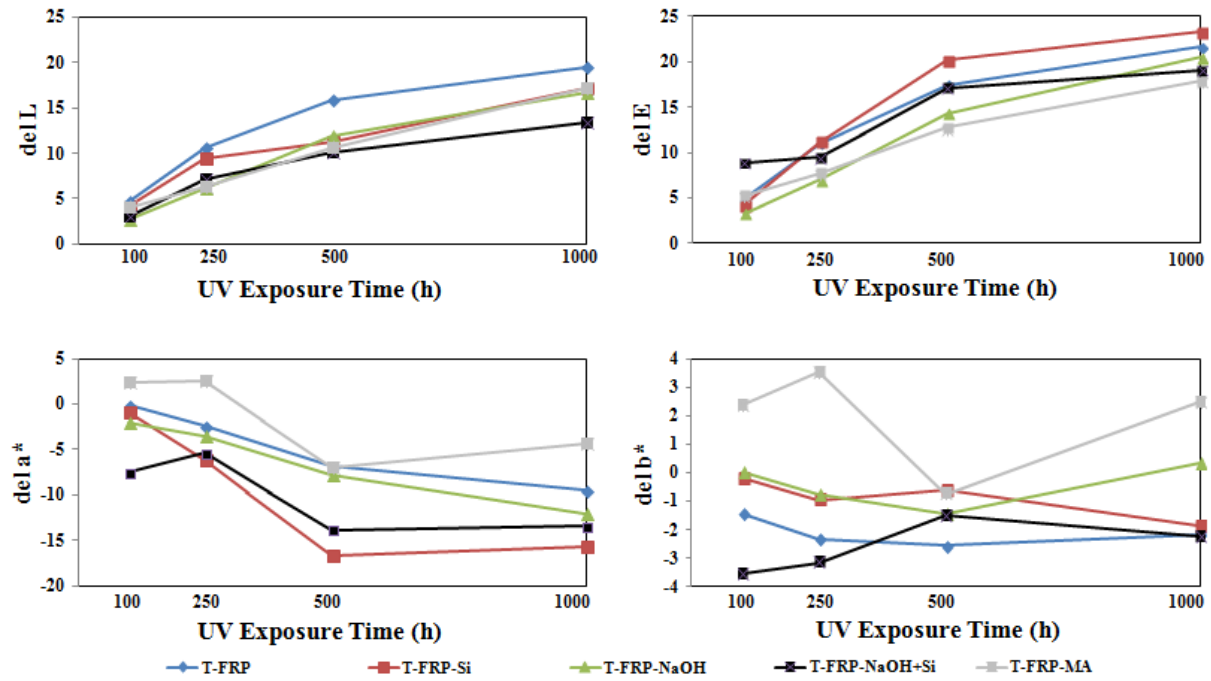
**Figure 9.** Evaluation of color measurement parameters with respect to UV exposure time

$\Delta L$ and $\Delta E$ values increased with increasing UV exposure time as changes in a* and b* have arisen and fallen for all composites. In general, the most noticeable color changes were observed during the UV weathering exposure of 500 hours. Increase in $\Delta L$ and $\Delta E$ values slowed down from 500 hours up to 1000 hours with UV weathering. As seen in Figure 9, the $\Delta L$ value of the untreated composite noticeably increased after 500 hours and reached the maximum value at 1000 hours compared to other composites. $\Delta L$ values of chemically treated composites show a similar trend up to 500 hours of UV exposure. However, less fading of composite surface occurred in composites with alkali-silane treatment after 1000 hours of UV radiation. Figure 9 shows that chemical treatments did not seem to affect the yellow-blue or red-green surface color in composites with weathering. The results for $\Delta a$ illustrate that composites have become green except composites with maleic anhydride, which tend to be blue after 1000 hours UV exposure period. Artificial weathering caused composites with maleic anhydride to become more yellow.

**Table 5.** Color parameters for pure LDPE matrix

| Color Parameter | UV Exposure Time (h) | | | | |
|---|---|---|---|---|---|
| | 0 | 100 | 250 | 500 | 1000 |
| a* | -0.2 | -0.25 | -0.5 | -0.3 | -0.5 |
| b* | -3.0 | -2.90 | -2.70 | -2.0 | -1.0 |
| L* | 82 | 83 | 84 | 86 | 86 |
| Δ E | - | 1.00 | 2.04 | 4.12 | 4.48 |

Color measurements for pure LDPE matrices were performed to understand the effect of the polymer matrix on the color changes for composite materials. Table 5 presents the results of color parameters for pure LDPE with respect to UV weathering time. UV radiation has a small influence on the discoloration of pure LDPE after 1000 hours of UV exposure time. These results suggest that cotton fiber structure has a major contribution on the color parameters for the composites. Pure LDPE surface acquired a yellow-green color with UV weathering. In Figure 10, the color change after 1000 hours of UV weathering can be explored for all samples.
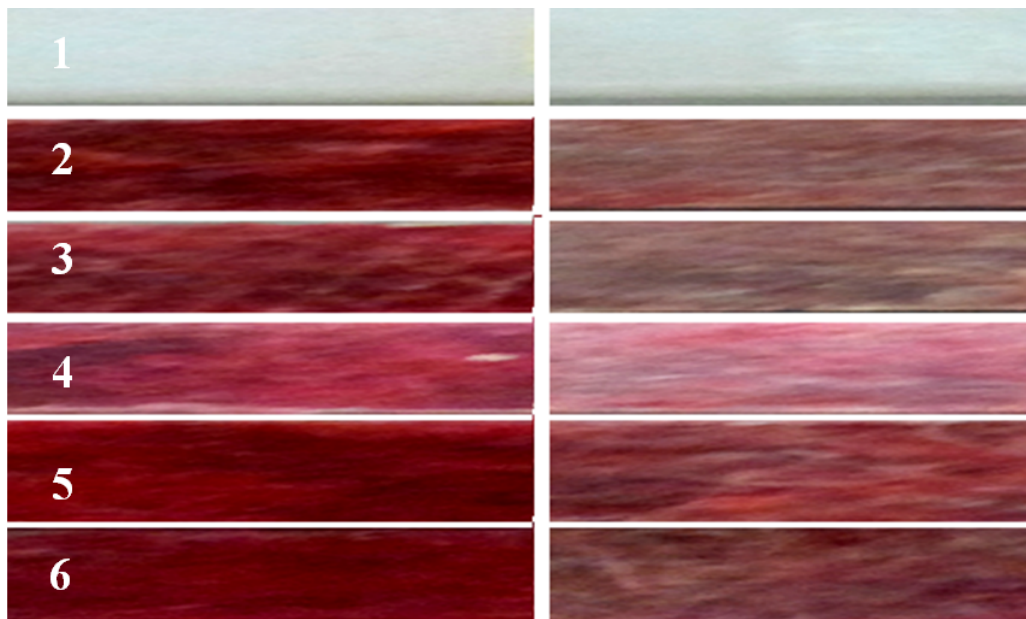


**Figure 10.** Surface colors for unweathered samples* (left) and samples* after 1000 h of UV weathering (rigth)
*1) Pure LDPE 2) T-FRP 3) T-FRP-Si 4) T-FRP-NaOH 5) T-FRP-NaOH+Si 6) T-FRP-MA

Another visual inspection in UV exposed composites was surface cracks. In Figure 11, the optical microscopy observations for unweathered and 1000-hour UV exposed composites were presented. As a result of UV irradiation, surface cracks can be seen on the surface of composite materials and supported by stereo microscope images. It is clearly noticeable that the surface of the composite have cracks after 1000 hours of exposure time, which may have

been responsible for the drop in mechanical properties. Composites showed surface degradation firstly after 500 hours of exposure time and the cracks increased with longer UV exposure.
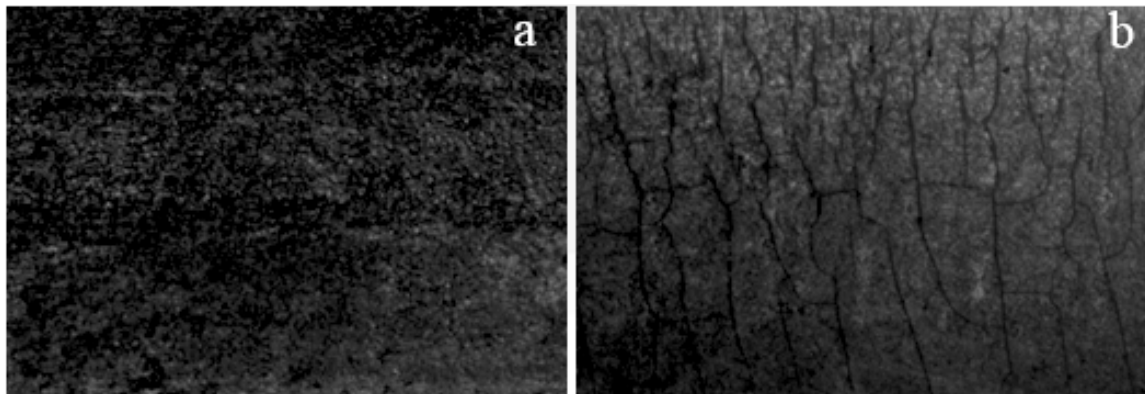


**Figure 11.** The surface of composites a)Unweathered b)After 1000 h of UV exposure

## 3.2 The effect of water absorption on the physical and mechanical properties

### 3.2.1 Physical properties

Figure 12 presents the water absorption and thickness swelling due to soaking time for untreated and treated composites. As seen in figure 12, water absorption occurs rapidly at the beginning of immersion; however, the absorption rate slows down over time. It is clear that chemically treated T-FRP composites show a decreasing rate of water absorption around 0.2~0.6% after 1000 hours of immersion compared to untreated T-FRP composites, and the extent of decrease varies and depends on the chemical treatment. As the fiber and matrix adhesion improved, the water absorption decreased due to strong interfacial adhesion that keeps the water molecules from moving into the composite structure. As seen in Figure 12, the composite with maleic anhydride and silane treated fiber shows lower water uptake values compared to the other composites. On the other hand, the composite with alkaline treated fiber shows a rapid water absorption after 500 hours and reaches highest water uptake value of 1.6% after 1000 hours of immersion. This result could be attributed to increased hydrophilicity by increasing fiber surface with alkaline treatment before manufacturing the composite, leading to more water uptake compared to others. These results were also observed for the wood fiber (WF) reinforced composite in the study conducted by Ichazo et al. They explored the effect of different treatments on the water uptake for WF reinforced composites and found that composites with alkaline treated fiber have the highest availability of OH groups in the particle surface. [44]. Among other various treatments, the degree of water absorption varies in the order: T-FRP-NaOH>T-FRP>T-FRP-NaOH+Si>T-FRP-Si>T-FRP-MA.
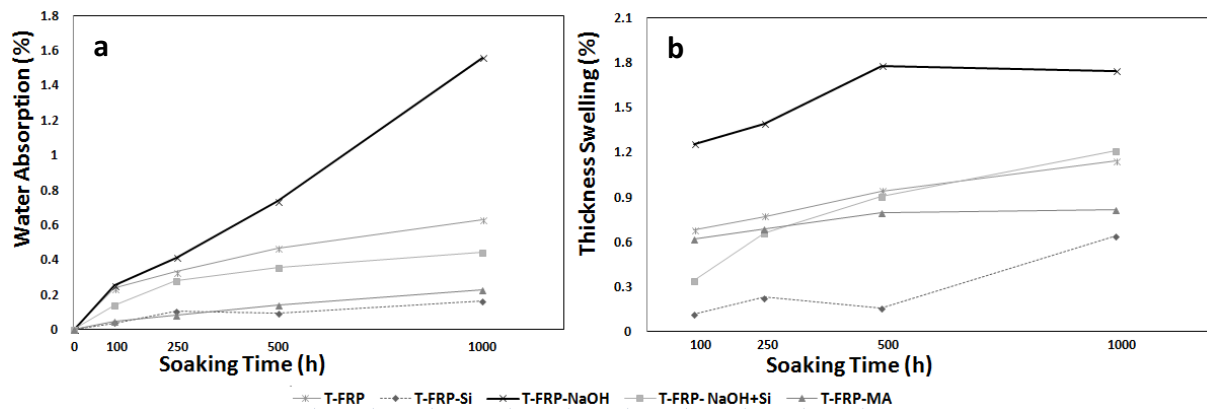
**Figure 12.** Effect of chemical treatments on the a) water absorption b) thickness swelling properties for composites

In addition, the swelling results show the same trend with water absorption results for all cases as seen in Figure 12. While the fiber/matrix interface is accessible to moisture from the environment, the cellulose fibers tend to swell. As a result of swelling of fibers surrounded by the polymer matrix, cracks may be formed at the matrix, causing the swollen fiber to flap.. This may also contribute to a reduction in the fiber/matrix adhesion.

### 3.2.2 Mechanical Properties

The effect of water absorption on the tensile properties of composites are shown in Figures 13 and 14. In general, the tensile properties of both untreated and chemically treated composites decreased after the moisture uptake. It is likely due to the effect of the water molecules penetrating inside and degrading the structure of the fibers, the matrix and the interfacial adhesion. In the case of untreated composite, tensile strength and Young's modulus decreased about 7% and 14% respectively (Table 6). For chemically treated composites, composite with alkaline treated fibers showed the lowest tensile properties after 1000 hours of soaking time compared to all composites as a consequence of highest water uptake performance which causes poor interfacial bonding and micro cracks for polymer matrix. However, composites with maleic anhydride exhibit the best tensile properties after 1000 hours of soaking time establishing a strong interface between cotton fiber and polymer matrix.
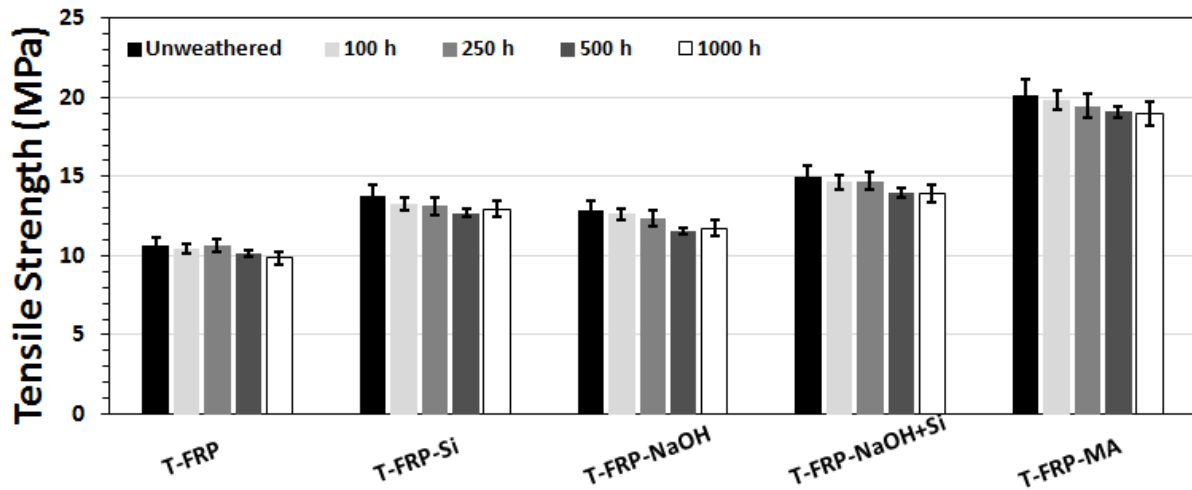
**Figure 13.** Effect of water immersion on tensile strength for untreated and chemically treated composites with respect to soaking time

As it can be seen in Figure 11, similar trends for YM values with tensile strength of composites were observed after water absorption. An exception was found for T-FRP composite with alkaline treatment, where YM values were almost stable up to 250 hours and decreased around 5-9% after 500 hours of water uptake. Reduction about 14% in YM values for T-FRP, T-FRP-Si and T-FRP-NaOH+Si composites were observed at the end of water immersion (1000 hours) while a 5% drop in YM for T-FRP-MA, which is the best material due to water immersion among the all composites, was observed after 1000 hours of water immersion. On the other hand, T-FRP-NaOH has shown the lowest YM values with water immersion due to higher availability of OH groups in the fiber surface compared to the other composites, which in turn contributes the water absorption and hence the poor adhesion between fiber / matrix as mentioned before. YM was found to decrease dramatically after 250 hours of aging with a continued drop up to 1000 hours of water immersion, with the greatest decrease from 443. 36 MPa to 346.71 MPa found for composite with alkaline treated cotton fiber (Table 6).
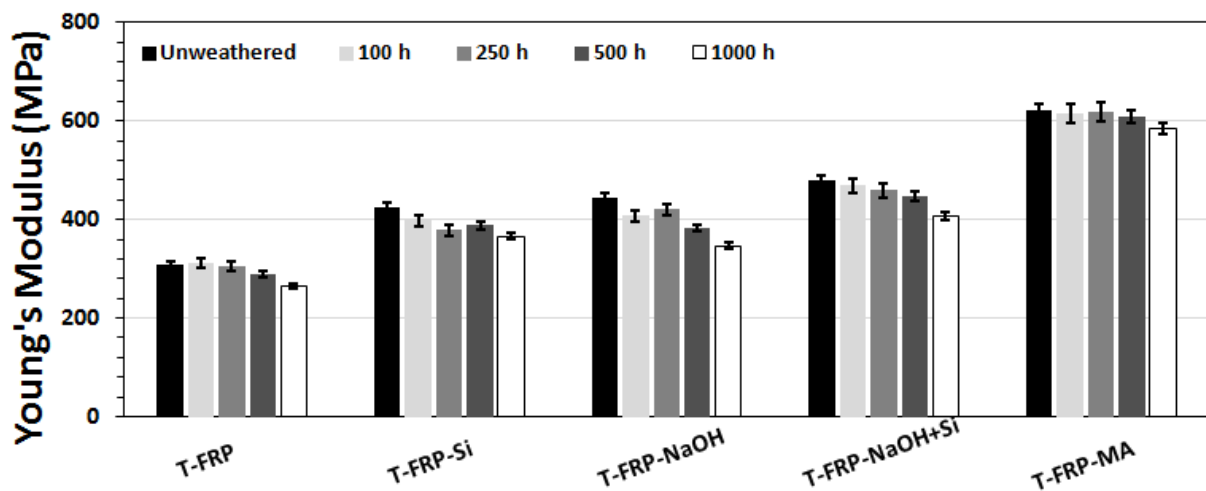


**Figure 14.** Effect of water immersion on Young's modulus for untreated and chemically treated composites with respect to soaking time

In Figure 15 and Table 6, one can easily observe the evaluation of impact strength (IS) for composites with respect to water absorption time. The change in IS with water immersion is more complex and likely to be more dependent on the treatment type compared to the change for tensile properties. It is worth noting that the IS of T-FRP, T-FRP-NaOH and T-FRP-Si were found to be increased with increasing water immersion time while IS of T-FRP-MA and T-FRP-NaOH+Si were found to be decreased as seen in Figure 15 and Table 6.
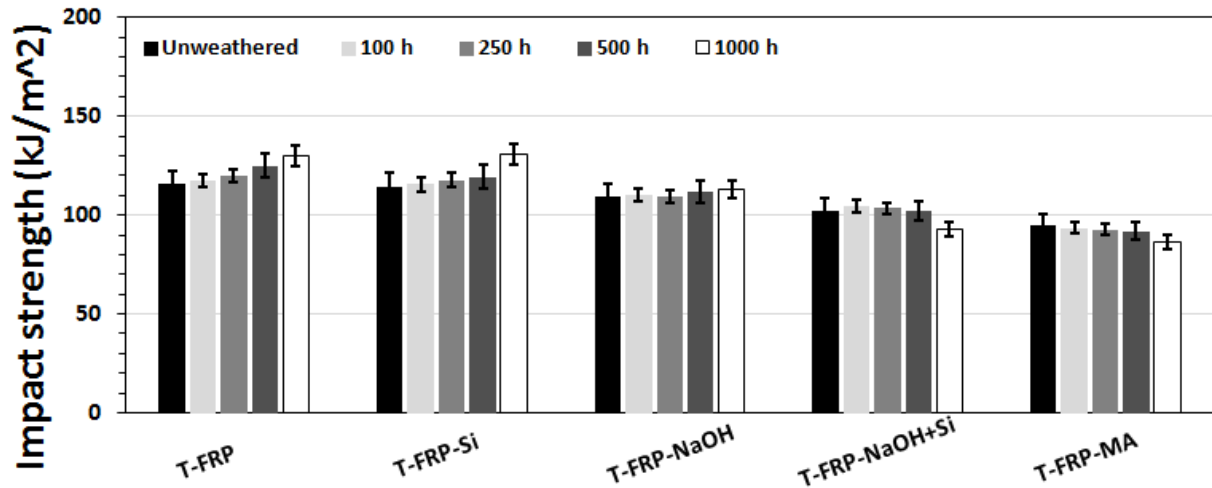


**Figure 15.** Effect of water immersion on impact strength for untreated and chemically treated composites with respect to soaking time

Different trends with various treatments in impact properties of composites with water absorption should account for two different reasons as follows.

- Degradation with water uptake might not affect the interfacial adhesion between fiber/matrix for T-FRP-MA and T-FRP-NaOH+Si composites; thus, the brittle characteristics of cotton fiber can occur more dominantly for IS behavior, although there might be some micro cracks resulted from fiber swelling after water absorption.
- On the other hand, increment in IS for T-FRP, T-FRP-NaOH and T-FRP-Si with water absorption due to degradation of interfacial adhesion which makes composites have more ductile characteristics of polymer matrix and water molecules trapped inside the composite structure with a plasticising effect [24].

**Table 6.** Change (%) of Tensile Strength (TS), Young's Modulus (YM), Impact Strength (IS) for composites with respect to water immersion time

| Change (%) | Materials | UV exposure time(h) | | | |
|---|---|---|---|---|---|
| | | 100 | 250 | 500 | 1000 |
| TS (%) | T-FRP | -1.42 | +0.28 | -4.63 | -6.89 |
| | T-FRP-Si | -3.63 | -4.72 | -7.99 | -6.03 |
| | T-FRP-NaOH | -1.72 | -3.60 | -10.03 | -8.69 |
| | T-FRP-NaOH+Si | -2.08 | -1.48 | -6.60 | -6.81 |
| | T-FRP-MA | -1.6 | -3.12 | -5.03 | -5.51 |
| YM (%) | T-FRP | +1.23 | -1.16 | -5.85 | -14.0 |
| | T-FRP-Si | -6.52 | -11.18 | -8.90 | -13.98 |
| | T-FRP-NaOH | -8.17 | -5.24 | -13.77 | -21.80 |
| | T-FRP-NaOH+Si | -2.41 | -4.32 | -6.70 | -15.98 |
| | T-FRP-MA | -1.05 | -0.59 | -2.18 | -5.89 |
| IS(%) | T-FRP | +1.48 | +3.61 | +8.16 | +12.08 |
| | T-FRP-Si | +1.02 | +3.05 | +4.31 | +14.09 |
| | T-FRP-NaOH | +0.66 | -0.21 | +2.22 | +3.53 |
| | T-FRP-NaOH+Si | +2.13 | +1.02 | -0.34 | -9.10 |
| | T-FRP-MA | -1.60 | -2.41 | -3.22 | -8.96 |

## 4. Conclusion

In this study, the effect of chemical treatments in order to provide better interfacial adhesion between the natural fibers and polymer matrix on the outdoor performance for T-FRP composites regarding UV exposure and water immersion weathering up to 1000 hours. To summarize, experimental results introduce the following conclusions.

- In TS values for the untreated and chemically treated composite samples, reduction between 10-15% was observed, which is less than the reduction in TS of pure LDPE after 1000 hours UV exposure time, due to the fact that composite samples have a lower amount of polymer subjected to the photo oxidative degradation.
- The highest overall drop in TS values was observed for composites with different chemical treatments compared to untreated composite with UV exposure. This result is likely due to degradation of fiber/matrix interfacial adhesion which is more predominant for the composites with treatment on the reduction of TS compared to untreated composite which has poor fiber/matrix interfacial adhesion already before weathering.
- For impact strength, it is interesting to note that chemically treated composites were affected less compared to untreated composites after UV exposure. This may be likely due to the degradation of fiber / matrix adhesion that results the composite to act more ductile during weathering.
- FTIR results showed that the chemically treated composites have lower stability than untreated T-FRP composites with longer UV exposure, the chemical groups which are more susceptible to oxidation for the chemically treated composites.
- All composite samples have shown surface degradation after 500 hours of UV exposure and the cracks seemed to be increasing with longer UV exposure.
- Chemically treated T-FRP composites showed a lower rate of water absorption around 0.2~0.6% after 1000 hours of water immersion compared to untreated T-FRP composite. The extent of drops varies with the chemical treatment. However, the

composite with alkaline treated fiber showed a rapid water absorption after 500 hours and reached highest water uptake value among all samples.

- Composites with maleic anhydride exhibit the best tensile properties after 1000 hours of soaking time, establishing a strong interface between cotton fiber and polymer matrix.
- The change in IS with water immersion was found to be more complex and also more dependent on the treatment type compared to the results for TS with water absorption.

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