# EFFECTS OF WEATHERING AND COMPOSTING OF FISH-SCALE-BASED EPOXY COMPOSITES

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## ABSTRACT

Bio-composting (BC) and natural weathering (NW) technique studied the degradation analysis of epoxy composites reinforced with fish scale (FS) particles. A fixed amount (15 wt.%) of FS was loaded into the epoxy to formulate the samples. The composites were dumped into the natural biomass waste and kept there for 49 days for BC analysis, whereas other samples were kept onto the soil in an open environment for NW for the same duration. A comparative analysis was performed before and after the degradation process. The samples were characterized by physical, mechanical, structural, thermal and morphological properties. The mechanical properties of the composites were characterized with the use of a universal testing machine and pendulum impact system. The scanning electron microscopy was utilized to observe the morphological properties. The thermal properties of the composites were characterized using thermo-gravimetric analysis and differential scanning calorimetry. Results showed a significant deterioration of the properties after the degradation of the composites. The tensile strength of the composites reduced due to BC and NW by 40 and 47%, respectively. The loss of thermal stability was significant. A significant amount of weight loss was occurred by both processes. The structural and surface property of the polymer was deteriorated.

***Keywords:*** Composites, Degradation, Curing of polymers

## 1. INTRODUCTION

In the past few years, bio-based materials have been widely exploited for the production of bio-composites [1]. Bio-filler reinforced polymer composites have attained the interest of researchers for the ecological demand. The environmental pollution drives scientists to produce new composite materials that are made from thermoplastics or thermosets polymer with natural resources as reinforcements [2-3]. Nowadays, the use of bio-based composites is continuously increasing in various products such as aerospace, automobiles, structural materials, consumer products and packaging materials. The eco-friendly bio-composites are designed to produce from renewable resources which has considerable degradability and improved bio-reintegration [4-5]. The bio-composites have huge application fields for their high mechanical properties, thermal properties, low cost, recyclability, availability and ease of maintenance [6]. The use of bio-composites is increasing in between 11% to 15% every year over last few years [7]. However, the market penetration and widespread acceptance of bio-composites has been limited for their non-structural applications, less durability for degradation and moisture absorbance in outdoor applications under harsh and changing environment.

The reinforcement of natural fibers into polymer matrix not only improves the mechanical and thermal properties of polymer-based bio-composites [8], but also retains the degradation of composites. Bio-composites have tendency to degrade when they are used in outdoor environments due to various factors such as UV radiation, moisture, microorganism and temperature [9]. The fiber reinforced composites, used in outdoor, absorbs UV light from the direct sunlight and the covalent bonds in the organic polymer are broken down with the effect of UV radiation. Thus, weathering of bio-composites is a great concern because photo degradation through weathering and composting has detrimental effect on the properties and appearance of composite materials. The harmful effect of weathering on the composites include degradation of artistic appeal for color fading and surface roughening, and physico-mechanical properties. Natural fiber reinforced polymer composites takes part in the degradation due to the UV light radiation and moisture during the weathering conditions. Chen et al. have shown that the flexural properties of the wood plastic composites decreased for the weathering conditions [10]. Chang et al. have analyzed the effect of weathering on the properties of the epoxy/glass fiber composites. Results showed that the fracture toughness of the composites decreased by 19% due to the exposure of UV radiation [11]. Kumar et al. [12] showed that the tensile strength of the epoxy/carbon fiber composites reduced by 29% under weathering condition compared to the control samples. The unsaturated polyester-based hybrid composites reinforced with kenaf blast and glass fibre became less thermally stable due to the weathering effect in natural environment [13].

Both UV radiation and moisture are responsible for decreasing the mechanical and thermal properties of the polymer composites. Photo-degradation of the composites takes place in presence of direct sunlight which is considered as primarily responsible source for damage of composite materials under ambient conditions. Usually, UV radiation in the range of 290 – 400 nm band in the sunlight initiates the degradation of polymer molecules in outdoor applications. The energy of UV photon (290–460 kJ/mole) is comparable to dissociate the covalent bonds of polymer molecules. The photo oxidative reaction occurs for the absorption of UV photons by polymer which alters the molecular structure of the polymers. The degradation of polymers take place through these chemical reactions causing chain scission and/or chain crosslinking [14]. For the chain scission from the chain structure of polymer, the molecular weight of the composites reduces. As a result, the mechanical properties and thermal properties of the composites are reduced. On the other hand, chain crosslinking of polymer causes the excessive brittleness and micro cracking of the composites. Photo-oxidative reaction can produce chromophores which is responsible for the discoloration of the composites if the visible light wavelengths are absorbed by the composites. Furthermore, if composite absorbs the UV radiation then an autocatalytic degradation reaction is occurred in the polymer molecules. Thus, the mechanical and thermal properties of the composites can be deteriorated due to the long-time exposure under UV radiation, especially harsh and changing adverse environment [15].

Moreover, moisture uptake also plays an important role on the durability of the natural fiber reinforced composites. Moisture can deteriorate the strength of the composites and de-bonding of the composites. Moisture absorption by polymer can change various properties of composites such as mechanical, thermal, and chemical properties depending on the chemistry of a polymer. Natural fibers of the composites absorb moisture which causes swelling of fibers. As a result, the interaction between matrix and fillers becomes weak which makes the surface of the composites unstable. Thus, micro-cracking causes in the composites, and consequently structural integrity and strength of the composites losses [16].

In this research, the bio-composites were prepared by reinforcing 15 wt.% of fish scale particles with epoxy. The combination of the fish scale as a bio-filler assists the degradation process. The mechanical, structural and the thermal properties of the composites were further verified the nature of the degradation process on both BC and NW. A necessity for prolonging their consumption is their biodegradability in natural environment where they may serve energy for various microorganisms. The biodegradability analyses were carried out through BC and by exposing the composites to NW. In NW, the composites were also exposed to direct sunlight, rain and moist environment. The surface topography, mechanical, thermal and structural properties, changes in lusters of the composites were analyzed.

## 2. EXPERIMENTAL

The local fish shops were the source of collecting fish scales those were later washed and cleaned to remove remaining dust and impurities. Then, the cleaned fish scales were left under sun light for drying. The dried fish scales were stored using the common zip bag until further used. To obtain a powder form fish scale, the fish scales were blended using blender. The powder form fish scales were sieved to separate the fine particles from the coarse residue. The epoxy resin, EPIKOTE™ Resin 240, was used as the polymer matrix for the composites. A curing agent, EPIKURE(TM) 3090, was used as the hardener for the composites.

The composites were prepared by mixing the fish scale particles and the epoxy. In this research, the amount of the fish scale particles was fixed by an amount of 15wt.%. A magnetic stirrer was utilized to stir the mixture at 250 rpm. The mixture was then cure using EPIKURE(TM) 3090 curing agent and casted onto a mold for further curing at ambient temperature for 24 hours. Finally, samples were taken out from the mold. The sample without filler was also prepared for further analysis. The samples were then taken out from the mold.

For bio-degradation analysis, three different samples, the neat epoxy (NE), raw fish scale (RFS) and the epoxy/fish scale composites (EFS), were subjected for multiple testing to compare the effect of the filler on the degradation. The degradation analysis was carried out by dumping the samples in waste-based biomass for bio-compositing and by exposing the composites to normal weathering. The NE, EFS and RFS were buried in soil with the biomass for bio-composting process. The weight of each sample were measured once every seven days. The weight loss was determined by the end of the analysis. The samples were bio-composted for 49 days. The structural, mechanical, thermal, surface topography and the color of the bio-composites were analyzed at the end of each period. For weathering, the samples were exposed to natural weathering conditions including sunlight, rain and moisture. The weight of each sample were measure once every seven days. The weight loss was determined by the end of the analysis. The sample were exposed to open environment continuously for 49 days. The weight loss of the samples was compared to determine the efficacy of degradation involving in both methods.

The mechanical testing was carried out to determine the mechanical properties of the composites before and after the degradation through bio-composting and weathering. The tensile testing of the composites was carried out using A universal testing machine, according to the ASTM D 638 standard method to test plastic in order to record tensile strength (TS) and tensile modulus (TM) of the samples. The flexural testing was carried out using A universal testing machine, LLYOD LR30K5 Plus, at 25 °C using the ASTM D790-97 standard to determine flexural strength (FS) and flexural modulus (FM) of the materials. The impact testing was carried out using the pendulum impact column, model: RAY-RAN, according to the ASTM D790-97 standard. The impact strength (IS) of the samples was determined before and after the degradation takes occur.

Thermogravimetric analysis (TGA) and differential thermal gravimetry (DTG) analysis were carried out by thermogravimetric analyzer, Mettler Toledo (model- TGA/DSC 1). Nearly 20.0 mg of the samples were placed in a platinum crucible for the testing. Test was conducted within the temperature range of 30 to 600°C under nitrogen atmosphere (flow rate: 30 mL $min^{-1}$). A constant heating rate of 20 °C/min was maintained during heating of the specimens. Differential scanning calorimetry (DSC) analysis was performed using differential scanning calorimeter, Mettler Toledo (model- TA-GC 10, Model: DSC 822e). About 20 mg of the samples were placed in a platinum cubicle for the testing. All tests were conducted within the temperature range of 30 to 600°C under nitrogen atmosphere (flow rate: 30 mL $min^{-1}$). A constant heating rate of 20°C/min was maintained during heating of the specimens.

To determine the weight loss of the neat epoxy and the composites, a regular check up on the weight loss was performed by a scale. The NE and composites were removed from the compositing and weathering environment after every 7 days. The samples were then washed thoroughly to remove excess dirt and let to dry. The final and the initial weight of the samples were recorded and the weight loss of the samples were calculated.

## 3. RESULTS AND DISCUSSION

The tensile strength (TS), tensile modulus (TM), and stress versus strain behavior of the composites are plotted in Figure 1a, 1b and 2, respectively. Figure 1 shows the TS of the composites before and after the natural weathering and bio-composting process. The TS of the NE and EFS composite was 19.83 and 17.81 MPa, respectively, before degradation. However, after degradation, the tensile strength for the NE for both weathering and composting drop to 19.73 MPa, which gave a marginally low reduction in tensile strength with only 0.5%, decrease. For EFS, the value of tensile strength after degradation through composting and weathering were 17.35 and 16.27 MPa, respectively. Based on the data obtain, the tensile strength of the EFS has dropped 2.58% via weathering and 8.64% via composting. The reduction of the tensile strength of the EFS composites can be related to the photochemical degradation, plasticizing effect and swelling effect. The fillers are swelled by absorbing moisture from environment which weaken the interface between the matrix and fillers. As a result, cracks are formed in the epoxy matrix [17]. The weathering and composting process may increase the surface roughness of the composites which causes the loss of fillers from the surface. For losing fillers from the surface, more water can be trapped inside the composites which acts as plasticizer [18]. For these reasons, the tensile strength of the EFS composites is decreased for both weathering and composting processes.

Figure 1b shows that the TM of the neat epoxy (NE) was 1170 MPa. After natural weathering and compositing, the value dropped to 943 MPa. The TM of the NE decreased by 19.3%. On the other hand, the TM of the composite before degradation was 1070 MPa, which decreased to 856 and 491 MPa, respectively, due to natural weathering and compositing. The TM of the EFS decreased by 19.9% and 54% due to natural weathering and bio-composting, respectively. Compared to the degradation of the EFS using natural weathering, the compositing showed higher efficacy. The EFS showed higher reduction in TM compared to the NE. In photo-degradation, ultraviolet radiation is absorbed by the peptide backbone of the protein which excites the electrons to higher energy states. The excited electrons react with the oxygen, absorbed from environments, to form peroxy radicals. The peroxy radicals play important role to degrade protein by reacting with the compounds of protein [19]. The degradation of fish scale in the composites reduces the tensile properties of the EFS composites.

Based on the Figure 2, the stress versus strain curve data for degradation through weathering and composting were discussed. From the graph plotted, data for NE was showing the highest stress value. The stress versus strain data curve shows that, the NE possessed the highest applied stress and strain before a break happen. However, after degradation took place, the stress versus strain data for NE decrease. The applied stress for both weathering and composting on NE were low as well as having a relatively lower strain before a break happen. This showed that the tensile properties for NE decline after a degradation took place. Meanwhile, for EFS, the stress versus strain data was much lower compared to that of NE before a degradation takes place. The applied stress is lower resulting to a lower strain before a break happen. However, after degradation took place, EFS undergo composting and weathering showing a gradual change on the stress versus strain. For the composting and weathering data, although the EFS required much longer time before a break happen compared to the EFS before degradation, the applied stress was relatively lower giving a much lower strain before a break happen compared to the applied stress on the EFS before degradation occur. This showed that the tensile properties for EFS decrease after degradation occur. The protein of fish scale absorbs UV radiation from sunlight and then starts to degrade the protein. UV radiation provides energy to the protein for the excitement of the electrons to higher energy singlet state. The higher energy state of electrons generates reactive oxygen species which cause the oxidation of amino acid of protein [19]. The oxidation process is also responsible for the degradation of epoxy where decomposition of hydro peroxides produces oxide ion to initiate the oxidation [20]. Thus, degradation of composites happens for the composting and weathering. As a result, the composites can withstand to lower stress when load is applied after degradation during the composting and weathering.

Figure 3 shows the data for flexural modulus and flexural strength before and after degradation. It was found that the flexural modulus for neat epoxy (NE) before degradation was 1520 MPa while the flexural modulus for the Epoxy/fish scale composites (EFS) was 1351 MPa. However, weathering and composting decreased to 1261 MPa and 1440 MPa, respectively. The decreasing in flexural modulus for the NE giving to 11.12% reduction for weathering and 5.26% reduction for composting. For EFS, the flexural modulus showed a decrease after degradation, being recorded 1307 and 849 MPa due to weathering and composting, respectively. The obtained data gave EFS a decreased as much as 3% through weathering and 37% reduction due to composting. Furthermore, referring to the flexural strength before and after degradation, both samples, NE and EFS were showing a decreasing trend in their flexural strength after degradation took place. Comparing to the method of degradation, it can be observed that the degradation through composting on EFS are showing a relatively high reduction compared when exposed to normal weathering. However, this result was totally opposite with NE. With only slight changes, NE are showing higher reduction when were exposed to normal weathering. Thus, this shows that degradation via composting was showing higher degradation efficacy compared to when the sample were exposed to normal weathering. Nevertheless, when comparing the samples, EFS were observed to be more favorable toward degradation than NE. EFS composites can absorb higher amount of moisture compared to the neat epoxy. Moisture uptake can accelerate the degradation process of the epoxy composites through the water diffusion and hydrogen ion exchange [21]. Thus, micro cracks are formed at the interface between the matrix and fillers at the surface. The micro-cracks formation at the surface reduces the Flexural properties of the composites [22].

Table 1 shows the impact properties of the samples. Through definition, impact properties signify the capability of a material to absorb and release energy when put under certain force [23]. Based on Table 1, the impact strength of both samples showed a decreasing trend of degradation. However, EFS shows a significant change after degradation took place. The epoxy-based composites absorb moisture during weathering from the environment. The absorption of moisture may cause localized defects which can lead to the reduction of the impact strength of the composites.

In this analysis, the degradability of the material was determined by measuring the weight loss of the composites during the degradation analysis. From weight of residual biodegraded Epoxy/fish scale composites (EFS) and Neat Epoxy (NE), it was understood that all weight loss was due to the degradation by the RFS. Figure 4 describe the graphical analysis of the percentage weight loss of the biodegraded sample after 49 days. In case of presence of fish scale as bio filler in the composites, it shows that the weight loss was high in both composting and weathering. However, for NE sample, it did not pronouncedly affect the weight loss during degradation in both composting and weathering. The reduction of weight loss of composites during composting and weathering can be described by the degradation through hydrolysis. Water from the surroundings enters to the polymer bulk which causes swelling. Water uptake by the epoxy initiates the chemical degradation by creating oligomers and monomers [24]. Pore are created at the surface of the composites for the progressive degradation of polymer, via which oligomers and monomers formed by degradation are released, leading to the weight loss of the composites. Thus, the overall weight loss of the epoxy-based composites was caused by the degradation of the weak chains of epoxy [25]. In addition, during the weathering condition, the weight of the composites may be reduced for the evaporation of water due to thermal effect. The weight loss of EFS composites is higher in weathering because the combination of moisture, temperature and light accelerate the degradation rate of the composites in the weathering condition.

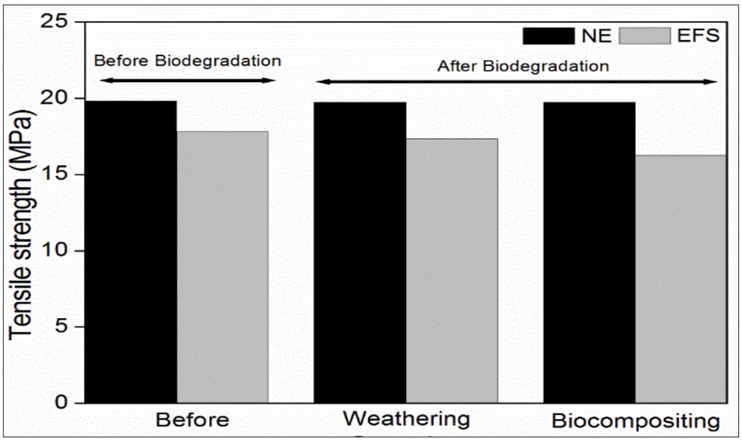
To understand the effect of bio-composting and natural weathering on the thermal behavior of the composites, the TGA, DTG and DSC were studied. From the analysis, the initiation of the degradation ($T_{onset}$), temperature at 50% weight loss ($T_{50\%}$) and char residue were recorded before and after degradation through bio-composting and natural weathering. Based on the data obtained from the TGA analysis (Figure 5), it was observed that the composites are thermally stable. The stability decreased after BC and NW. However, the epoxy/fish scale composites showed significant decrease in the thermal stability on both BC and NW compared to the NE. As the FS exhibited the lowest stability after undergo BC and NW, it can be clarified that the presence of the FS particles on the composites are subjected to the significant deterioration on the thermal properties of the samples. The thermal properties are listed in Table 2. From the data obtain, it can be observed that the thermal properties degrade after weathering and composting takes place. This is due to composting and weathering process that have already pre-degrade the organic material from the composites [26]. In addition, ultraviolet photons in the range of 290–400 nm absorbed by the polymers can degrade greatly the polymer molecules that may cause the thermal stability to deteriorate [27]. The direct ultra-violet radiation to the surface of the composites altered the physical chemistry of the polymer causing the composites to degrade [28]. Thus, resulting to the composites having low thermal stability after weathering and composting.

Based on Figures 6 and 7, it was observed, at 50% weight loss, the temperature for the epoxy/fish scale composites (EFS) was the highest compared to neat epoxy (NE) and raw fish scale (RFS). The glass transition temperature $T_g$, crystallization temperature $T_c$ and melting temperature $T_m$ also decrease after composting and weathering. Meanwhile, after degradation, EFS were having relatively lower thermal resistance than before degradation take place. This indicates that the samples required less temperature to reduce 50% of its weight. The bond between the composites weakened enough to break the bond between the composites under lower temperature. From the $T_g, T_c$ and $T_m$, the temperature decreased for all samples after degradation take place. However, this value varies according to samples. RFS having relatively higher value for $T_g, T_c$ and $T_m$ followed by the EFS. Thermal properties of the EFS composites were decreased for the harsh environment. Moisture and UV radiation are mainly responsible for the degradation of composites in the compositing and weathering condition. In addition to that, the photo-degradation reaction takes place on the composites via direct sunlight caused the thermal stability to deteriorate [23-24]. The direct ultra-violet radiation to the surface of the composites altered the molecular chain structure by chain scission of polymer causing the composites to degrade. Chain scission reduces the molecular weight of epoxy, giving rise to decrease in thermal stability [27]. As the composites have different thermal expansion from one another, the photo degradation reaction cause by ultraviolet radiation from sunlight accelerate the deterioration of the thermal properties, causing the $T_g, T_c$ and $T_m$ to degrade [29-32]. Thus, resulting to the composites having low thermal stability after weathering and composting. It is found that the char residue of EFS composites before BC and NW is 6.4%. Later, the char residue of EFS composites was found 6.1% and 5.6%, respectively, after composting and weathering. The char residue obtain after composting for the epoxy/fish scale composites are the lowest after composting and weathering test. Meanwhile for the raw fish scale (RFS), the char residue after the end of the analysis are showing the highest residual.

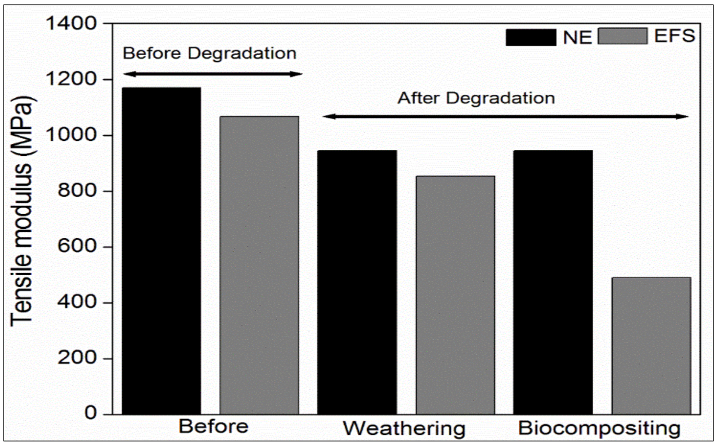
From Figure 8, it can be seen that both neat epoxy and epoxy/fish scale composites turn to dark brown colour after exposing 7 weeks of natural weathering. The brown color of the composites become dull after 49 days of natural weathering testing. This is due to the direct ultraviolet radiation from the sun to the surface of the sample. According to Abdullah et al., the change in color is known as bleaching in photo degradation when a material is exposed to UV radiation. The changes in color is an important factor which aid the matrix to degrade and cause the sample to become brittle [33]. This is due to the presence of the FS in the composites. The presence of the organic material on the composites boost the pho-oxidation degradation which allows the initiation of chemical reaction to form free radical for leading the chain scission cleavage. Due to different thermal expansion between the NE and the FS, it weakens the interaction between the NE and the FS [34]. Thus, the mechanical properties of the composites are deteriorated. From natural weathering, it can be observed that the surface of the composites become rougher compared to the NE. This is because, upon exposure of natural weathering, the samples are exposed to weathering conditions, the sample surface started become rough. This indicated the formation of small cavities in the surface resulting from the removal of the FS particles from the surface [35]. The existence of this small cavities weakened the adhesion between the matrix and composites causing the mechanical properties to be reduced. This explain why the mechanical and thermal properties of the composites are lower compared to the neat epoxy.

## 4. CONCLUSION

This study investigated the effects of natural weathering and composting on the FS-filled epoxy composites. The UV radiation, moisture, heat and cold effects and micro-organisms were the stimulators to facilitate the degradation of the FS which ultimately affect the properties of the epoxy composites. The epoxy/fish scale composites were prepared and buried in the bio-waste/soil for composting, and exposed to normal environment for natural weathering. The properties of the composites before and after compositing and natural weathering test were studied. The tensile, flexural and impact properties of epoxy/fish scale composites were decreased both for bio-compositing and natural weathering tests. The thermal properties of the composites were also reduced after the composites undergo the bio-composting and natural weathering conditions. The combination of weather, temperature, humidity, and degradation process significantly weakens the interfacial adhesion between the matrix and fillers which leads to the reduction in tensile, flexural and impact strength of the composites. This investigation indicates that the incorporation of fish scales into the epoxy matrix accelerate the degradation of the composites when they are exposed to UV radiation, moisture and in contact with micro-organism.




(a)




(b)

Figure 1: Tensile strength (a) and tensile modulus (b) of the composites.

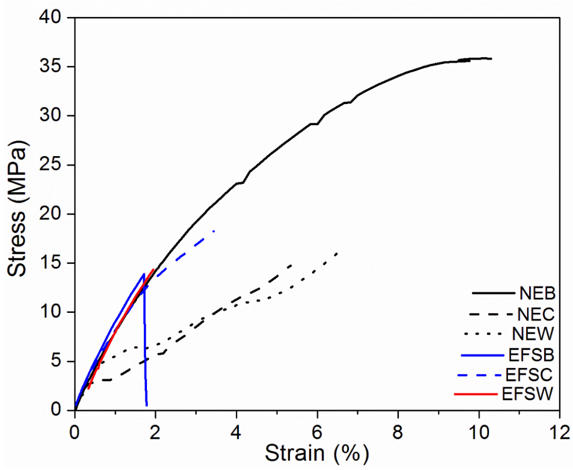
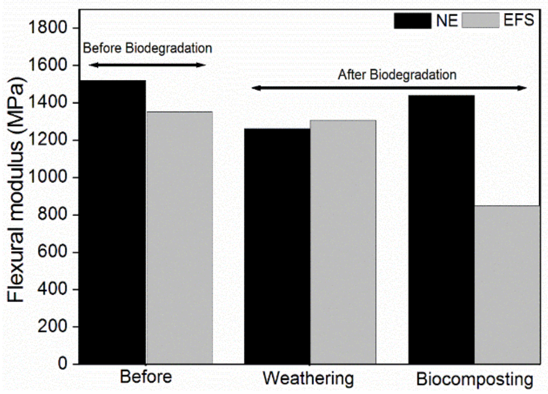
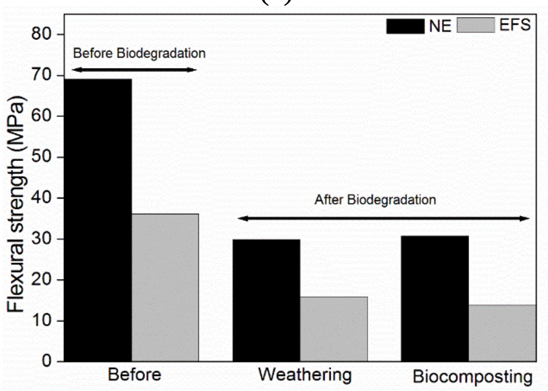



Figure 2: stress vs. strain curves of the sample.




(a)




(b)

Figure 3: Flexural modulus (a) and flexural strength (b) of the composites.

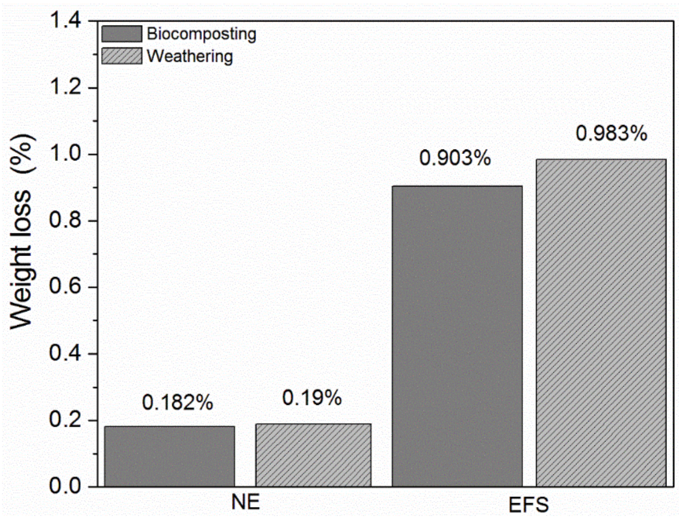



Figure 4: Weight loss of the samples due to weathering and composition.

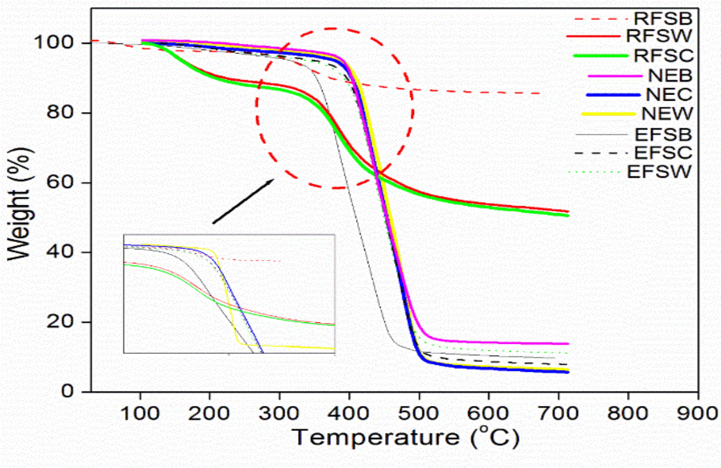



Figure 5: TGA curves of the samples.

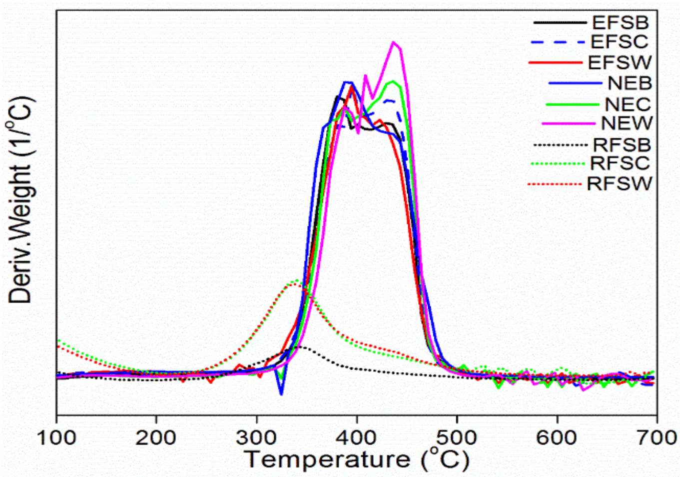



Figure 6: DTG curves of the samples.

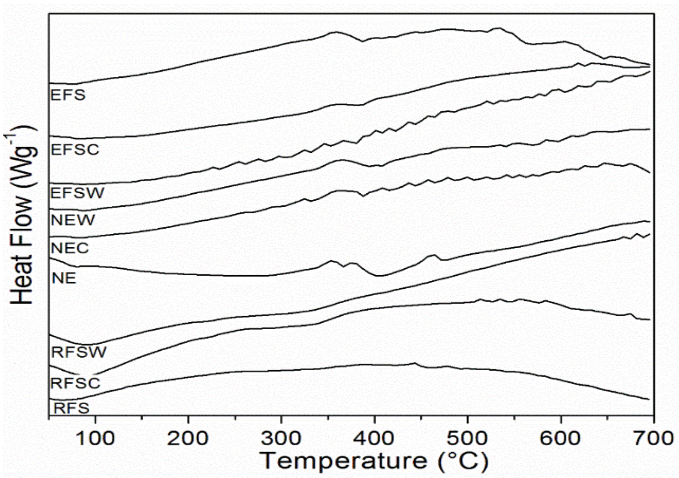



Figure 7: DSC thermograms of the sample.

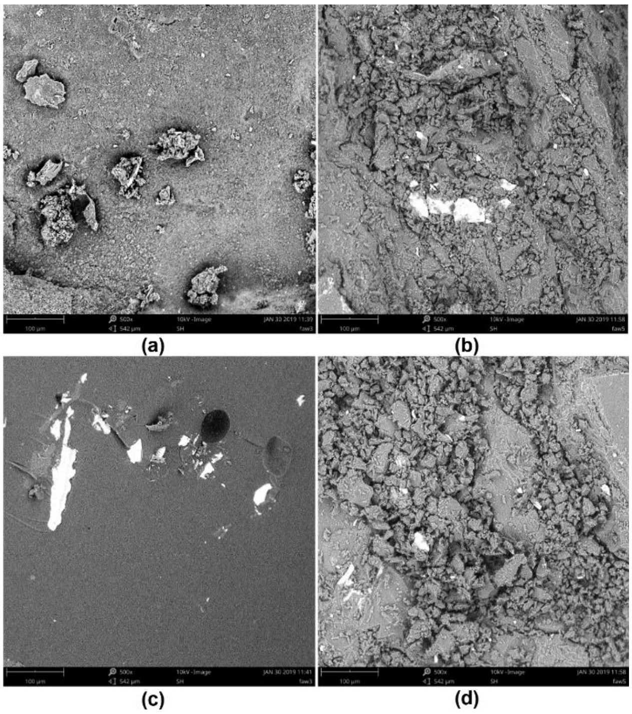



Figure 8: SEM image of the samples.

Table 1: Nomenclature of the samples with their impact strength before and after the degradation

| Method | Percentage filler | Impact Strength (kJ/m$^2$) |
|---|---|---|
| Before degradation | 0% | 5.9134 |
| | 15% | 2.9114 |
| After Composting | 0% | 4.339 |
| | 15% | 2.1379 |
| After Weathering | 0% | 3.1262 |
| | 15% | 2.7967 |

Table 2: Thermal properties of the composites before and after the degradation.

| Sample | $T_{onset}$ ($^oC$) | $T_{50\%}$ ($^oC$) | $T_g$ ($^oC$) | $T_C$ ($^oC$) | $T_m$ ($^oC$) | Char Residue (%) |
|---|---|---|---|---|---|---|
| NE Bef | 248 | 407 | 349 | 351 | 402 | 10.4 |
| NE Com | 241 | 384 | 347 | 360 | 384 | 11.7 |
| NE Weath | 205 | 392 | 344 | 360 | 392 | 8.6 |
| EFS Bef | 268 | 574 | 346 | 359 | 574 | 6.4 |
| EFS Com | 261 | 384 | 340 | 350 | 384 | 6.1 |
| EFS Weath | 225 | 410 | 243 | 246 | 378 | 5.6 |
| RFS Bef | 142 | - | 432 | 441 | 454 | 85.1 |
| RFS Com | 79 | - | 370 | 388 | 399 | 53.7 |
| RFS Weath | 72 | - | 362 | 395 | 414 | 52.3 |

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