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Impact of Weathering on the Mechanical and Weight Reduction Properties of High-density Polyethylene (HDPE) Composites Filled with Treated and Untreated Eggshell Powder (ESP) Fillers

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Abstract: *The impact of weathering on the mechanical and weight reduction properties of untreated and treated high-density polyethylene/chicken eggshell powder (HDPE/ESP) composite was investigated. The tensile properties of HDPE/ESP composites with and without chemical modifications, which have been exposed to outdoor environment under certain duration is been characterised by a light weight tensile tester under different ESP filler loadings. The results show that as the period of exposure increases, the tensile strength, tensile modulus, and elongation at break decreases. In addition, it is observed that the composite exhibits gradual weight loss with weathering periods compared to pure HDPE. As the filler loading increases, the percentage of weight loss also increases. Treated HDPE/ESP filler composite experienced higher weight loss than untreated HDPE/ESP filler composites. The presence of silane coupling agent in the treated ESP enhanced the dispersion of ESP in HDPE and thus increases the interfacial interaction and adhesion between HDPE and ESP. Enhanced dispersion of treated ESP reduces the weathering resistance of HDPE composites.*

Keywords: high-density polyethylene, eggshell powder, silane coupling agent, tensile strength, weathering

1. INTRODUCTION

Developments of polymeric materials have greatly reduced the consumption of finite natural resources in many industries.[1] Among the polymers, polyethylene is one of the most important materials that have been widely used in engineering, construction, sports, domestics, and packaging applications.[2] The most common types of polyethylene are high-density polyethylene (HDPE) and low-density polyethylene (LDPE) with a range of density of 0.94–0.96 and 0.91–0.94 g cm^{-3}, respectively.[3]

Currently, to fulfil the demand for polyethylene in polymer applications, various additives are found to be compounded with polyethylene. Additives such as fillers, plasticisers, antioxidants, stabilisers, and flame retardants are added into polyethylene for the purpose of achieving specifications and requirements of an application. Among the additives, filler reinforced polymer composites have been used to modify the properties of polymer, which is desired to be better than the neat polymer. In order to improve the mechanical and thermal properties of neat polymer, the polymer is usually compounded with mineral fillers such as talc, mica, and calcium carbonate.[4]

Due to the environment issues on sustainability, utilisation of finite sources for material science has shifted to renewable sources.[5] Non-biodegradability of conventional fillers such as talc, calcium carbonate, and china clay has been seeking replacement by renewable source. The advantages of using fillers from renewable source includes reducing emission of pollutant, easy processing, low cost, and reduced dependence on natural resources based derivation products.[6] In recent years, natural fillers obtained from animals and plants are used as reinforcement for thermoplastics with low melting point. Apart from utilisation of waste, low hardness of natural fillers reduces abrasion to processing equipment.[7]

Despite of having significant benefits, there are some major questions about the long-term durability and environmental performance of composites sample filled with fillers from renewable resources. The external environment can be harmful due to moisture, acid rain, and thermal fatigue.[8] Ultraviolet (UV) radiation exposure can also reduce the overall performance of polymers and reinforcing fibers.[9] Thus, the main objective of this paper is to investigate the effects of weathering on mechanical and weight reduction properties of HDPE/eggshell powder (ESP) filler composites. The outcome of this research will provide information on the applicability of using HDPE/ESP composites in outdoor environment.

2. MATERIALS AND METHOD

2.1 Materials

Eggshells were collected from restaurants in Kampar, Perak. HDPE resin was supplied by Lotte Chemical Titan (M) Sdn. Bhd. (Johor, Malaysia), while (3-mercaptopropyl)trimethoxysilane coupling agent (MW = 196.32 g mol^{-1}) was purchased from Sigma Aldrich (M) Sdn. Bhd. (Petaling Jaya, Selangor, Malaysia) and n-butanol was purchased from Orionor Hightech Sdn. Bhd. (Cyberjaya, Selangor, Malaysia).

2.2 Preparation and Surface Treatment of ESP

Eggshell was washed in running tap water to remove any contaminants on its surface. The membrane in the inner shell was removed using hand. The eggshells were then left to dry overnight at room temperature to remove excess water. Then, the eggshells were blended using Waring Laboratory Blender model HGB 2WTS3 (NE Scientific Enterprise, Kuala Lumpur, Malaysia) to smaller pieces and dried in Memmert GmBH Universal Oven, model U, supplied by Interscience Sdn. Bhd. (Shah Alam, Selangor Malaysia) at 100°C for 5 h.

The dried eggshell was grinded to powder using Ultra Centrifugal Mill ZM200 from Retsch GmbH (Haan, Germany). The grinded samples were then sieved using 0.1 μm mesh W.S. Tyler's RO-TAP® Sieve Shaker model RX-29-10 (EverGreen Engineering and Resources, Semenyih, Selangor, Malaysia).

For the treated samples, the dried ESP was subjected to surface treatment in a suspension containing 30 g of eggshell with 30 ml of n-butanol. The amount of silane added to the stirred suspension is 2 wt. % relative to the mass of filler.[10] The mixture was stirred for 3 h and the slurry was left standing for five days. The solvent was filtered and removed using Buchner funnel. Remaining eggshell on the filter paper was dried and collected.

2.3 HDPE/ESP Composite Compounding

Two different types of composites, i.e. HDPE with treated ESP (HDPE/ESPM) and HDPE with untreated ESP (HDPE/ESP) were prepared using melt blending technique in an internal mixer, model Brabender Plastograph EC 815652 from Brabender GmbH & Co KG (Duisburg, Germany). The composites with 10, 20, 30, and 40 phr ESP loading were prepared. Processing temperature, rotor speed of internal mixer and processing time was set to be 150°C, 60 rpm, and 10 min, respectively. The composites were moulded to test specimens using the Hydraulic Moulding Press, model GT-7014-H, supplied by GOTECH Testing Machines Inc. (Taiwan) at temperature of 150°C and compression pressure of 20 MPa. The moulding cycle includes 5 min of preheating, 2 min of pressing, followed by 2 min of cooling. The samples were cooled inside the mould using chilled water circulation.

2.4 Characterisation and Testing

Untreated and treated ESP were subjected to Fourier transform infrared spectrometer (FTIR) analysis. The infrared (IR) spectrum of raw materials was recorded using Spectrum RX1 Perkin Elmer (Petaling Jaya, Selangor, Malaysia) analyser. KBr pellet technique was applied. The samples were mixed with dried KBr powder and pressed to small pellets. The spectra were recorded from 4,000 to 400 cm^{-1} wavelength with 32 scans.

Weathering test was carried out to study the effect of exposure to natural weather on the weight loss and tensile properties of HDPE/ESP composites. Dumbbell shaped samples was prepared in accordance with ASTM-D638 standard. The pre-weight samples were exposed to natural atmosphere at the roof of Block E in Universiti Tunku Abdul Rahman, Perak Campus using a weathering board. The samples were taken out in three different period of time, namely, 15, 30, and 45 days and weighed. The weight loss due to weathering was calculated using Equation 1.

$$\text{Percentage of weight loss (\%)} = (W_1 - W_2)/W_1 \times 100\% \quad (1)$$

where W_1 and W_2 are the weight of the sample before and after weathering, respectively.

Tensile test for HDPE/ESP composite were carried out using Universal Testing Machine (WDW-5Y Single Column, TINIUS OLSEN, Balakong, Selangor, Malaysia). The test was conducted in accordance to ASTM-D638 standard. The test was carried out at a pulling rate of 50 mm min^{-1}. Tensile strength, modulus, and elongation at break were recorded after the sample was weathered.

3. RESULTS AND DISCUSSION

The FTIR spectrum of ESP in Figure 1 shows the absorption bands of carbonate at 875 and 1,412 cm^{-1}. According to Deshmukh et al.[11] and Abdolmohammadi et al.[12], the absorption peak of calcium carbonate is reported at 873 cm^{-1}, which is close to 875 cm^{-1}. The presence of these bands proves the carbonate content within ESP. The peak of modified ESP between 1,200 and 1,600 cm^{-1} becomes sharper after the modification with silane. Study conducted by Phueakbuakhao et al. show that the stretching vibration in the range of 1,250–950 cm^{-1} assigned to polysiloxane structure, indicating the presence of silane coupling agents in the filler.[10]

Figure 2 represents the percentage of weight loss at different filler loadings under different interval weathering period. From Figure 2(a–c), it shows that as the filler loading increases, the percentage of weight loss also increases. HDPE/ESPM composite experienced higher weight loss than HDPE/ESM. However, the overall weight loss is less than 0.5%. Thus, all the samples are quite stable up to 45 days.

Figure 3 represents the comparison of weight reduction at different duration of weathering for untreated and treated HDPE/ESP composites. Figures 3(a) and (b) show that the composite exhibits gradual weight loss with weathering periods. The increment of weight loss after a long period of exposure to natural weathering is due to the oxidation and chain scission of HDPE polymer matrix due to UV lights.[13] As a consequence, polymer chain hydrophobicity and molar mass decreases, which in turn increases the bioavailability that cause the polymer to become susceptible to biodegradability by bacteria in air.[14] Biofiller such as ESP can facilitate the growth of bacteria and this increases the biodegradable activity on the surface of HDPE. As the interaction between the HDPE and ESPM is better compared to HDPE with ESP, the biodegradation is higher in HDPE/ESPM composites. This leads to higher weight loss in HDPE/ESPM composites.

Figure 4 represents the tensile strength of (a) untreated and (b) treated HDPE/ESP composites after weathering test. From Figure 4, it can be summarised that as the filler loading increases the tensile strength decreases. For untreated and treated HDPE/ESP composite, it shows that both composites exhibit higher tensile strength than the pure HDPE at 10 and 20 phr filler loading with optimum tensile strength obtained at 10 phr filler loading. In comparison with untreated HDPE/ESP composites, treated HDPE/ESPM composites exhibit higher tensile strength at all filler loadings. This is because the presence of coupling agent promotes a better adhesion between the inorganic and organic components. When the composite is weathering for a longer period of time, the tensile strength decreased more. This

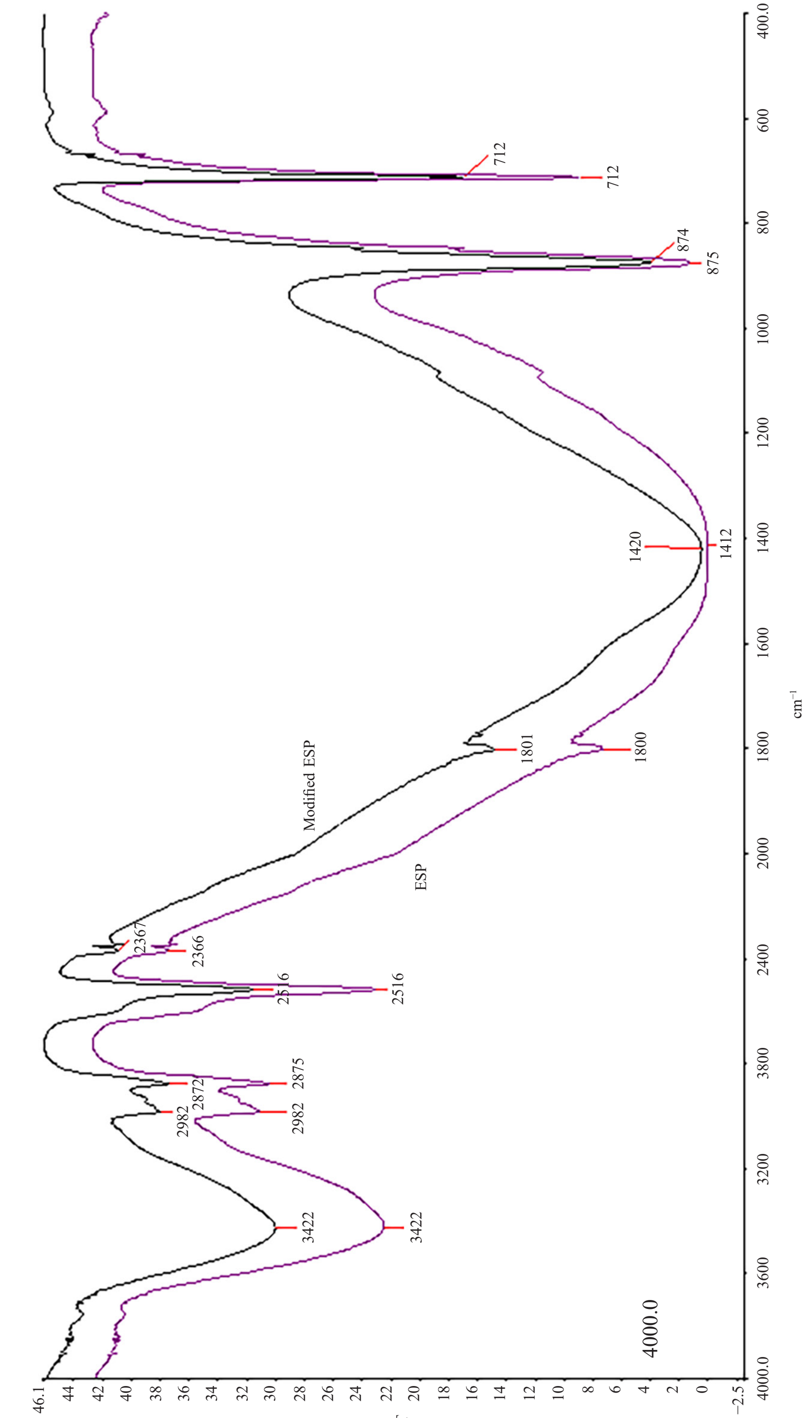


Figure 1: FTIR spectra of ESP compared with modified ESP silane.

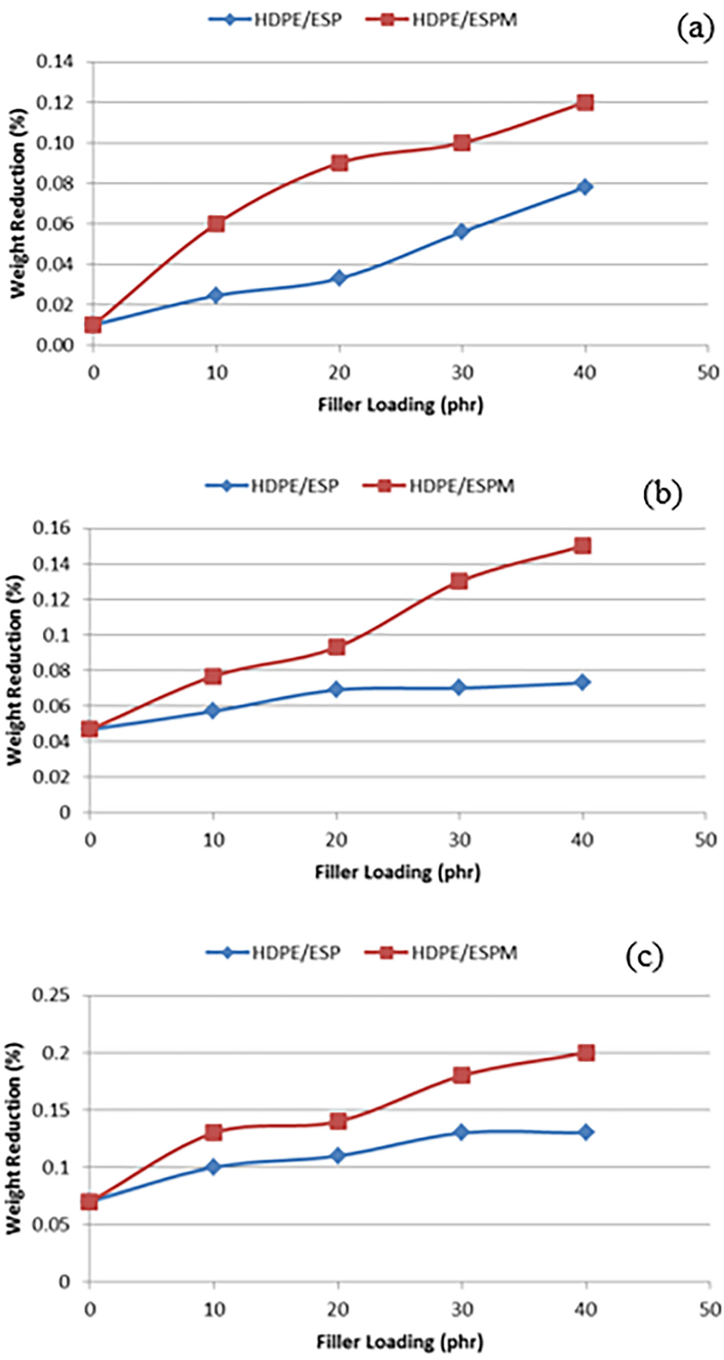


Figure 2: Weight reduction of weathering sample after (a) 15 days, (b) 30 days, and (c) 45 days.

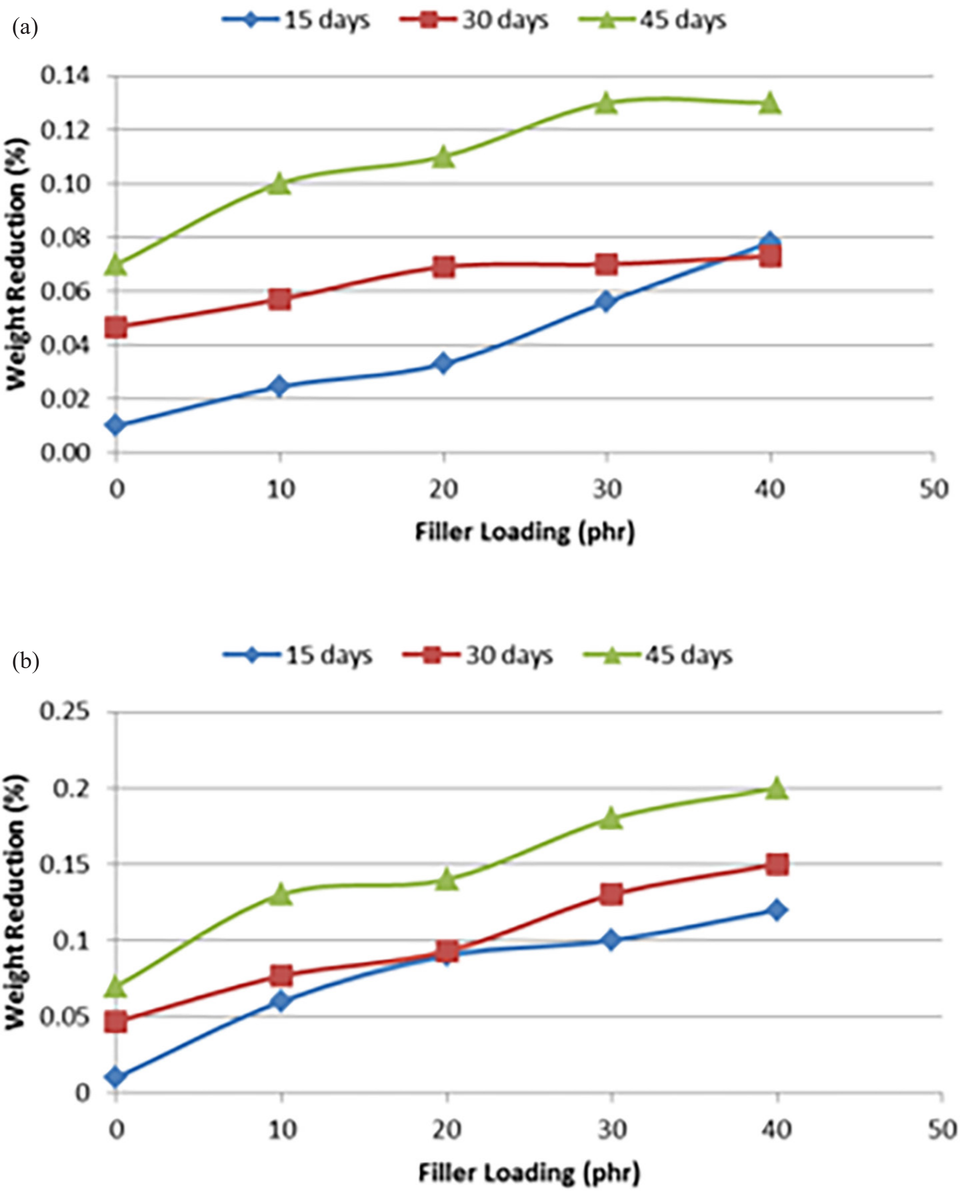
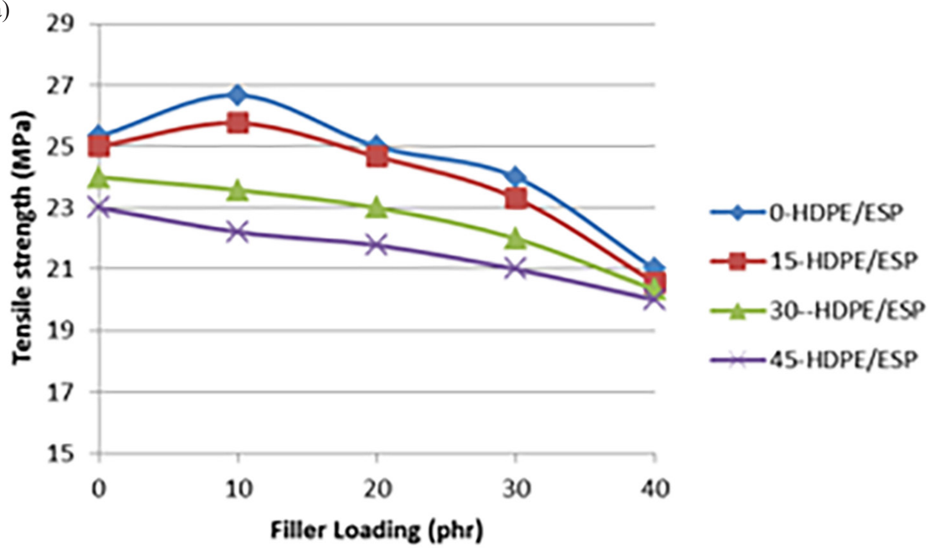


Figure 3: Comparison of weight reduction at different duration of weathering for (a) HDPE/ESP and (b) HDPE/ESPM composite.

(a)



(b)

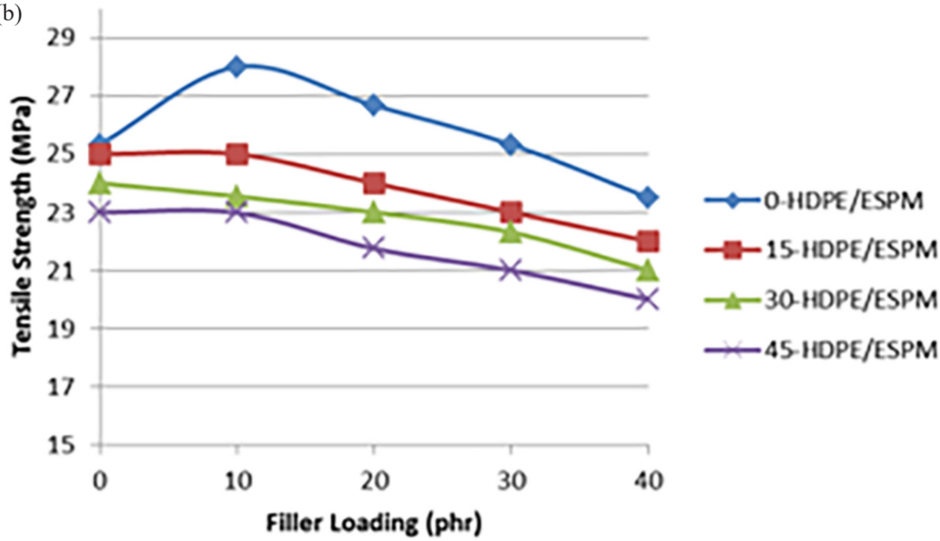


Figure 4: Tensile strength comparison after weathering in (a) untreated and (b) treated HDPE/ESP composites.

is because when the composite is exposed to the environment, it is also exposed to the presence of the UV light where this UV light penetrates in the composite and attacks the composite polymer chain. It breaks the polymer chain and causes the interfacial adhesion bonding between the matrix and the filler to become weak. Therefore, the longer the composite is exposed to the UV light, it will cause the interfacial adhesion bonding between the matrix and resin to become weaker and directly reduce the tensile strength of the HDPE/ESP composite. Overall, the treated HDPE/ESPM composite enhance better tensile strength compared to untreated HDPE/ESP composite. This is due to the presence of coupling agent that enhances the interfacial adhesion bonding between the matrix and filler compared to untreated HDPE/ESP composite.

Figure 5 represents the tensile modulus of untreated and treated HDPE/ESPM composites after weathering test. From Figure 5, it shows as the filler loading increases, the tensile modulus also increases for both untreated and treated HDPE/ESP composites. The increment of tensile modulus at higher filler loading indicates that the composites are stiffer at higher filler loading. From Figure 5, it can be seen that the tensile modulus of HDPE/ESP composite for both untreated and treated composites are higher that the pure HDPE matrix. This is because ESP filler has stiffer characteristics compared to HDPE matrix resin.[15] The composite filled with treated ESP filler has higher modulus than untreated ESP filled composite at all filler loading with optimum results achieved at 10 phr loading. The higher tensile modulus for treated HDPE/ESP filler composite is due to better interfacial adhesion between the HDPE polymer chain and treated ESP filler. Good interfacial adhesion will interlock the polymer chain on the surface of the filler, thus, the mobility and deformability are restricted by the stiff particles of ESP and cause increment in stiffness of the composites.[16,17] It can be concluded from the results that treated HDPE/ESP filler composite exhibits better tensile modulus compared to untreated HDPE/ESP filler composite.

Figure 6 represents the elongation at break of untreated and treated HDPE/ESP composites after weathering test. The importance of conducting elongation at break test is to determine the ductility of a specific material. It can be observed that as the filler loading increases, the elongation at break decreases for both of the composites. In addition, the elongation at break decreases more as the HDPE/ESP composites are exposed to weathering for longer period compared to shorter period of time. The filler loading has restrained the HDPE chains movement and resulting in the presence of highly localised strain, which cause dewetting between the matrix and filler. Thus, the HDPE matrix becomes stiffer and less ductile. As a result, the composite toughness and resilience reduce and lead to lower elongation at break.[18] From Figure 6, it shows that the treated HDPE/ESP filler composite has

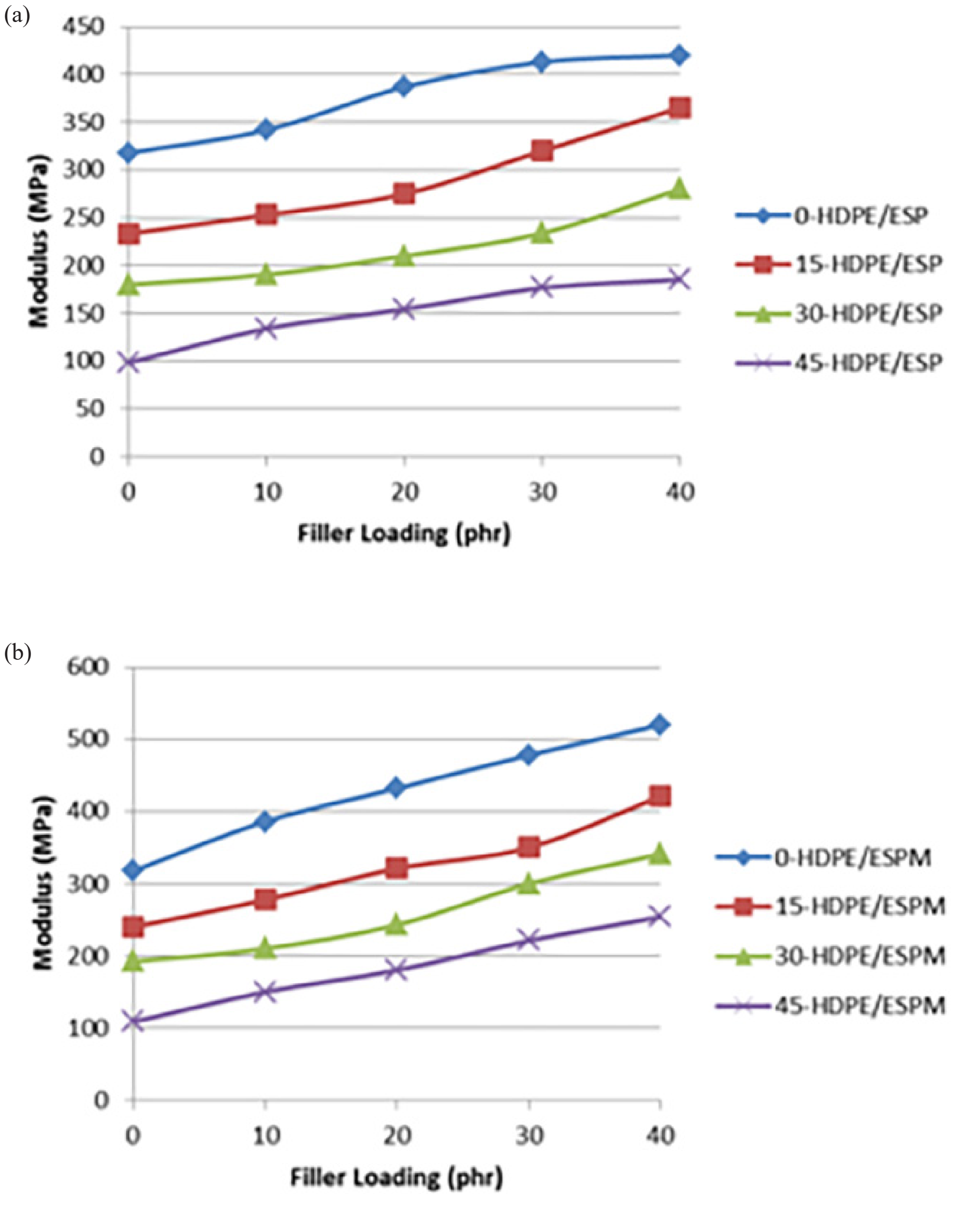


Figure 5: Tensile modulus after weathering in (a) HDPE/ESP and (b) HDPE/ESPM composites.

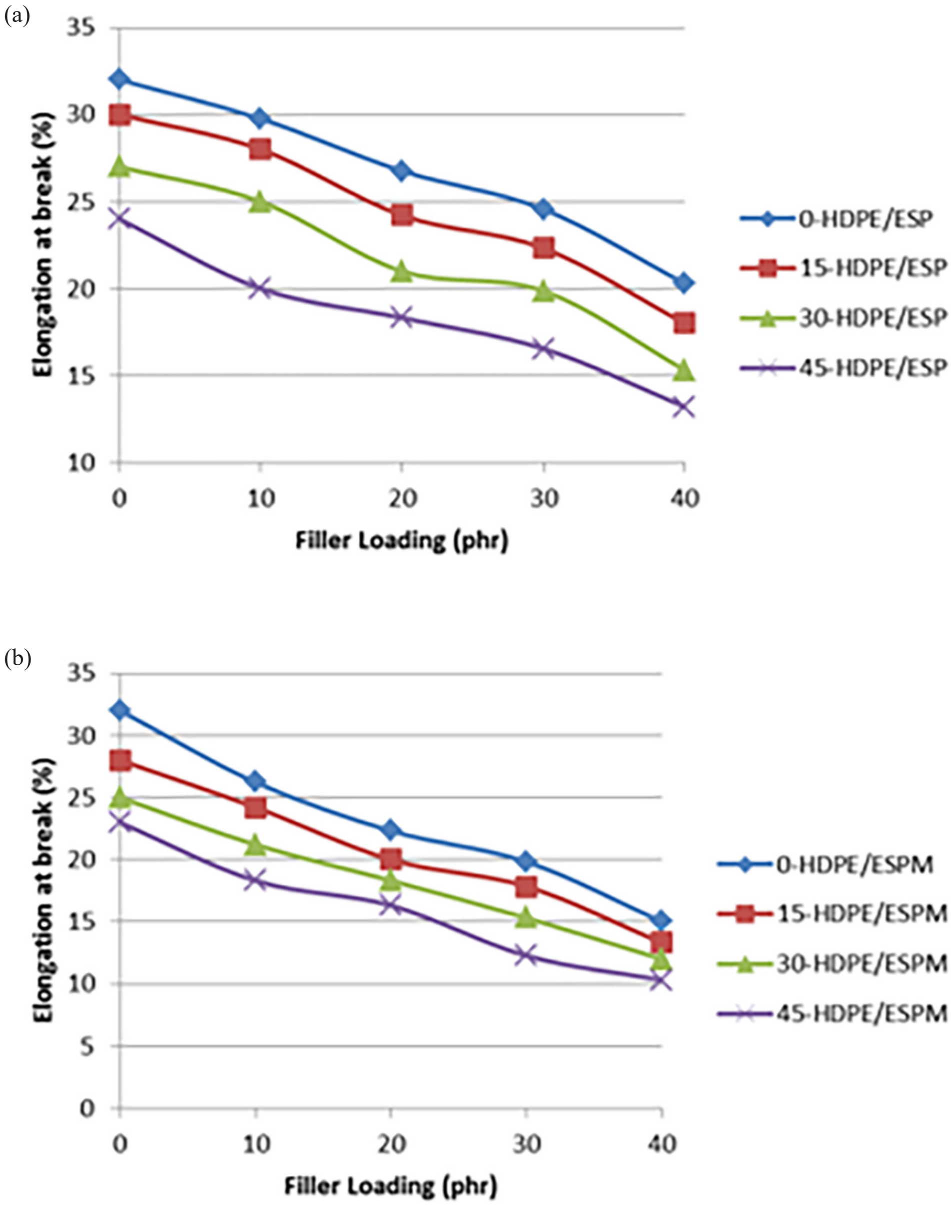


Figure 6: Elongation at break of samples after weathering in (a) HDPE/ESP and (b) HDPE/ESPM composites.

lower elongation at break compare to untreated HDPE/ESP filler composite at all filler loadings and weathering period. Moreover, as the exposure time increases, HDPE/ESP filler composite samples have lower percentage of elongation at break compared to the non-weathering sample. This is due to the fact that as the presence of UV light increases, the radiation from the UV light attacked the polymer chain, which caused the composites to become more brittle compared to the samples exposed at shorter period of time. As shown in Figure 5, the tensile modulus for treated HDPE/ESP filler composite exhibit higher tensile modulus compared to pure HDPE and also HDPE/ESP filler composites. Increment of tensile modulus due to demobilisation of polymeric chain on filler surface will cause decrement in ductility and elongation at break. Such a reduction in elongation at break of a polymer composite with increment of tensile modulus has been reported by Igwe and Onuegbu, Nwanonenyi and Chike-Onyegbula, and Nwanonenyi et al.[19–21]

4. CONCLUSION

In this paper, the impact of weathering on the mechanical and weight reduction properties of untreated and treated HDPE/ESP filler composites were investigated. The results show that the tensile strength and modulus is lower for untreated HDPE/ESP filler composites due to the incompatibility of hydrophilic filler to hydrophobic matrix. Therefore, surface modification on ESP filler proved to effectively increase the interfacial adhesion and resulting in the improvement of tensile properties as compared to pure HDPE. When the samples were exposed to weathering, the tensile properties reduced gradually with exposure period. The percentage of mass reduction increased as the filler loading of composite increased. However, the mass reduction is 0.2 wt. %, which is very low even for the samples that were exposed the longest period of weathering for 45 days. The tensile strength, tensile modulus, and elongation at break decreases as the samples were exposed under longer period of time. This is because the presence of UV light radiation breaking the HDPE polymer chain and in the same time less agglomeration is observed for treated HDPE/ESP filler loading at higher filler loading compared to untreated HDPE/ESP filler loading.

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