

Accelerated weathering properties of compatibilized composites made from recycled HDPE and nonmetallic printed circuit board waste

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ABSTRACT: The main aim of this work is to examine the influence of the contents of nonmetallic printed circuit board (PCB) waste component on the photodegradation of recycled high-density polyethylene (rHDPE) composites. The properties tested were chemical changes, flexural properties, color stability, water absorption, leaching properties, and crystallinity changes of the composites after exposure to 2,000 h of accelerated weathering. Surface degradation for composites with nonmetallic PCB was less compared to unfilled rHDPE mainly because glass fibers covered almost the whole surface of specimens, acting as a protective layer, thus, slowing down the photodegradation reaction. Incorporation of compatibilizer in rHDPE/PCB composites had played an important role in resisting degradation due to UV exposure. All the composite samples became lighter in the early stages of weathering exposure; however, compatibilized composites showed less lightening and reduction on strength and modulus. Carbonyl index increases with exposure time indicating that the oxidation reaction continuously occurred during the aging process. Incorporation of compatibilizer had successfully reduced the water absorption uptake by the composites and effectively delayed some degradation properties of weathering. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43110.

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INTRODUCTION

In the previous studies conducted, nonmetallic PCB waste has been recycled in a safe and environmentally sound manner by applying encapsulation technique in preparing composite materials.^{1,2} High-density polyethylene (HDPE) was used to create a coating or jacket over the nonmetallic PCB waste. Several studies were also conducted to study methods to reuse the nonmetallic waste as filling material in some practical products such as in producing nonmetallic plate,³ construction materials.^{4,5} Recovered nonmetallic PCBs were also used to make models, construction materials, composite boards, sewer grates, and amusement park boats.⁶ The nonmetallic PCB products have better mechanical characteristics and durability than traditional materials and fillers. Recently, composite materials are gaining attention as one of the potential fields in development and application. Most researchers are engaging in utilizing nonmetallic fractions obtained from PCB recycling process into plastics to produce composite materials. At present, the recovery of the

PCB waste uses the physical technique, which mainly emphasizes on converting the nonmetallic PCB waste into filler materials in the application of various fields.⁷ Although their physical recycling applications are interesting, all of them are focused mainly on mechanical, thermal and leaching properties testing. So far, no studies have been conducted to investigate the weathering properties of composites made from recycled HDPE and nonmetallic PCB waste material. Moreover, most of the studies done to utilize these filler materials are just at the stage of laboratory research, less in application. Thus, this current research is seen important to investigate the suitability of the composite materials intended for outdoor applications. This article mainly aims at investigating the structure–property degradation of compression molded nonmetallic PCB and recycled HDPE (rHDPE/PCB) composites with and without compatibilization under accelerated weathering exposures. The purpose of the test is to subject specimens to intensive representative outdoor conditions. Other tests assess the chemical changes,

mechanical properties, color stability, and leaching properties of the composites after the exposures. The results were used to determine the influence of nonmetallic PCB filler content on the ability of the composites to resist UV light irradiation for outdoor applications.

EXPERIMENTAL

Materials

Virgin HDPE. The Virgin HDPE (vHDPE) of injection molding grade (Titanvene™ HD5218EA) was obtained from Titan Polyethylene, Johor, Malaysia. The melt mass flow index (MFI) and density of HDPE are 18 g/10 min and 0.950 g/cm³, respectively.

Recycled High-Density Polyethylene. Recycled HDPE (rHDPE) used in this work was supplied by Metahub Industries Sdn Bhd, Johor. The rHDPE is from postindustrial HDPE pipe waste. The HDPE pipe was recovered and shredded into small flakes with 8–10 mm sizes. The MFI and density are 7 g/10 min (190°C, 2.16 kg) and 0.916 g/cm³, respectively.

Nonmetallic Printed Circuit Boards (PCBs) Waste. The nonmetallic PCB used as a filler material in this work was an industrial solid-waste byproduct from PCB recovery process obtained from METAHUB Industries Sdn Bhd (Johor, Malaysia). This was in the form of powder and without electronic elements. The nonmetallic PCBs with particle size of <0.3 mm were selected for making composites. The density of the nonmetallic PCB waste is about 1.7 g/cm³.

Maleated Polyethylene (MAPE) Compatibilizer. The maleated polyethylene (MAPE) compatibilizer used was OREVAC® 18365 supplied by Arkema. Orevac® 18365 resin is a maleic-anhydride-modified LLDPE designed for the coextrusion of multilayer barrier structures providing outstanding adhesion between the layers. The melt index and density are 2.5 g/10 min and 0.916 g/cm³, respectively.

Compounding and Preparation of Composites

Blends of rHDPE and nonmetallic PCBs were premixed in sealed containers and shaken manually. The rHDPE and the nonmetallic PCBs were dried at 80°C for 24 h prior to compounding and both were compounded using Brabender Plastocorder PL 2000 counter-rotating twin-screw extruder with a screw length/diameter of 25:1, to a continuous high output (~3–6 kg/h). The barrel temperature profile adopted during compounding was 210°C at the feed section, decreasing to 200°C at the die head with fixed screw-rotation speed at 50 rpm. The extruded materials were compression molded by hot-press machine into mechanical properties testing specimens with operating temperature of 200°C with 15 min of preheat and another 10 min for compression, followed by cooling process at room temperature for 5 min before removing it from the mold.

Measurement of Properties

The test samples were mounted in Q-Sun Xenon Test Chamber and subjected to a cycle of exposure, as recommended by ASTM D 4329-05. The cycle of exposure was set at 8 h of UV exposure at 70°C and followed by 4 h of condensation at 50°C. These cycles were continued for 2000 h. Samples were removed

for optical, color, and flexural tests. The color coordinates for each composite were measured for three replicate samples before and after exposure to the accelerated weathering during the UV exposure at preset exposure times, using a method outlined in ASTM D2244. A Spectrophotometer (Minolta CM-2500d) was used to measure the color according to the Commission International d'Eclairage (CIE) color system (CIE 1976). L , a , and b were measured for three replicate samples and the color change, and ΔE_{ab} was determined by eq. (1). L^* is used to represent the lightness, and a^* and b^* are the chromaticity coordinates.

$$\Delta E_{ab} = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2} \quad (1)$$

Where ΔL , Δa , and Δb represent the difference between initial and final values of L^* , a^* , b^* , respectively.

Water absorption test was conducted according to ASTM D570-98 using the immersion method for 2 and 24 h of immersion period. Water absorption rate was determined by eq. (2) below:

$$\text{Water Absorption Rate} = [(W_s - W_d)/W_d] \times 100\% \quad (2)$$

Where, W_s = saturated weight of samples (kg) and W_d = weight of samples (kg).

Fourier-Transform *Infrared Spectroscopy* (FTIR) spectra were recorded in the range of 400–4000 cm⁻¹. The resolution has been set at approximately 4 cm⁻¹ with three numbers of scan for each sample. The purpose is to determine the carbonyl index which represents the amount of carbonyl compounds produced in the photo-oxidation process. The carbonyl index has been calculated with the following formula [eq. (3)] from the data obtained after recording FTIR spectra of the composite materials.

$$\text{Carbonyl index} = \frac{I_{1718}}{I_{2912}} \quad (3)$$

Where I represents the peak intensity. The peak intensities were normalized using the peak at 2912 cm⁻¹, which corresponds to alkane CH stretching vibrations of the methylene groups. This peak was selected as a reference because it changed the least during weathering.

Flexural test was done according to ASTM D790 by EZ 20KN LLYORD universal testing machine under ambient conditions. The cross-head speed of 3 mm min⁻¹ was used with a support span of 100 mm. Five specimens of each formulation were tested and the average values were reported.

A differential scanning calorimetry (DSC7-Perkin Elmer) test was also carried out to study the crystallization and melting behavior of composites. DSC performed by heating composite samples of about 6–12 mg. The samples were heated at a rate 10°C/min from 30 to 250°C. Three specimens of each formulation were tested and the average values reported. The percentage of crystallinity X_c was calculated using the following eq. (4):

$$\% \text{ Crystallinity} = 100\% \times \frac{\Delta H_m}{f \Delta H_{m, \text{ideal}}} \quad (4)$$

where ΔH_m is the measured heat fusion, f is the weight fraction of the component in question, and $\Delta H_{m, \text{ideal}}$ is the enthalpy of fusion for 100% crystalline.

Table I. Chemical Composition of Nonmetallic PCB

Compound	Percentage (%)	Compound	Percentage (%)
CaO	18.98	MnO	-
SiO ₂	43.24	TiO ₂	0.44
Al ₂ O ₃	9.17	P ₂ O ₅	0.06
SO ₃	0.33	Sb ₂ O ₃	-
Br	6.53	SrO	0.14
CuO	5.83	ZrO ₂	0.02
BaO	0.50	ZnO	0.02
Fe ₂ O ₃	0.77	As ₂ O ₃	0.01
Na ₂ O	0.14	Cr ₂ O ₃	-
Cl	0.06	MoO ₃	-
SnO ₂	0.05	Rb ₂ O	-
MgO	0.52	NiO	77 ppm
K ₂ O	0.16	PbO	5 ppm

Nonmetallic PCBs mainly consist of epoxy resin, glass fibers, and a small concentration of metals.

The morphology of the samples was examined by using FESEM to analyze the surfaces of the samples upon weathering exposures using fractured surfaces. Prior to the analysis, the fractured surfaces of the specimens were sputter coated with a thin layer of gold.

Preparation of Samples for Toxicity Characteristic Leaching Procedure (TCLP) Test

For TCLP test, 100 g of samples were added to approximately 2 L of extraction fluid following the USEPA standard TCLP method USEPA 1992. The mixing ratio of extraction liquid to sample was 20:1. The solution was spinned for 18 h with a rotation of (30 + 2) rpm in a National Bureau Standards leaching machine. On completion of the test, the solution was filtered using a borosilicate glass fiber filter size 0.6–0.8 μm with 50 psi pressure. This process must be done immediately after the sample was collected. The samples were subsequently analyzed by using the Inductively Coupled Plasma (ICP-MS). Sample blanks and spikes were also performed to ensure accurate measurements.

RESULTS AND DISCUSSION

Chemical Composition Analysis of Nonmetallic PCB

The nonmetallic PCB powder was quantitatively analyzed for chemical composition using X-ray Fluorescence Spectrometry (XRF) and the result is shown in Table I. Nonmetallic PCBs mainly consist of epoxy resin, glass fibers, and a small concentration of metals. The nonmetallic PCBs contained approximately 72.7% of glass fiber materials with SiO₂ at the highest content of mass which is 43.2%, 6.7% of metallic materials, and 6.5% of organic resin material containing Br. Other elements existed only in small amounts in the range of 0.44% to 5 ppm.

The presence of nonmetallic PCB was further determined via FTIR testing. In the infrared spectrums (FTIR) of Figure 1 which was obtained from the nonmetallic PCB powder, a number of absorption bands can be seen. The absorption bands and

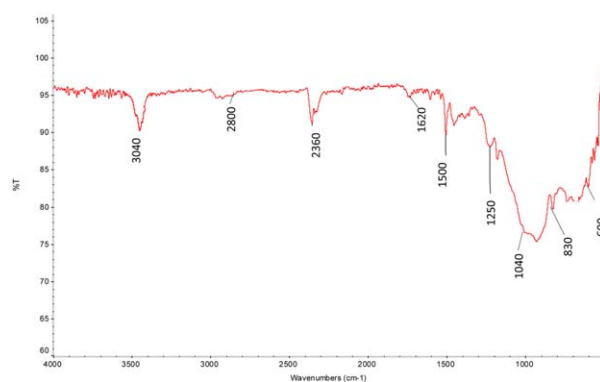


Figure 1. Infrared spectrum of nonmetallic PCB material. The FTIR spectra showed that the waste PCB was resin polymer with a little fiberglass. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

its frequencies are tabulated in Table II. The result showed that the waste PCB was resin polymer with a little fiberglass, and its polarity was due to the presence of hydroxide groups, carbonyl groups, acetal groups, and silanol groups on the particle surfaces.⁹ Meanwhile, the metal oxide particles also absorbed water vapor in the air and contribute to the polar functional groups.

Composition of Recycled HDPE

During recycling, the purity of materials was often unpredictable, leading to variations in properties. The variation in properties between rHDPE and vHDPE is attributable to the existence of impurities. In the recycling process, packaging material is one of the most common contaminants.¹⁰ The matrix material used in this work, rHDPE, was obtained from the plastic recycling plant. The composition of the rHDPE was determined via FTIR testing. The spectra of the same are shown in Figure 2.

Polyethylene is the main content of the sample from the peaks at 2915 and 2848 cm⁻¹. There is also a small peak near 1719 cm⁻¹ indicating that the rHDPE has gone some degradation. The integrated area between 1730 and 1710 cm⁻¹ of the absorption band at 1719 cm⁻¹ was used to determine the oxidation degree, carbonyl index. The influence of processing

Table II. Absorption Bands and Its Frequencies for Nonmetallic PCB Waste

Absorption band	Frequency (cm ⁻¹)
O-H stretch	3400
C-H stretch	2800-3000
C-C stretch	1500-1620
Phenyl-oxygen stretch	1250
C=O stretch	1040
C-H bend	829
Si-O stretch	1000-1110
C-Br stretch	800-600

Waste PCB is a resin polymer with a little fiberglass, and its polarity was due to the presence of hydroxide groups, carbonyl groups, acetal groups, and silanol groups on the particle surfaces.

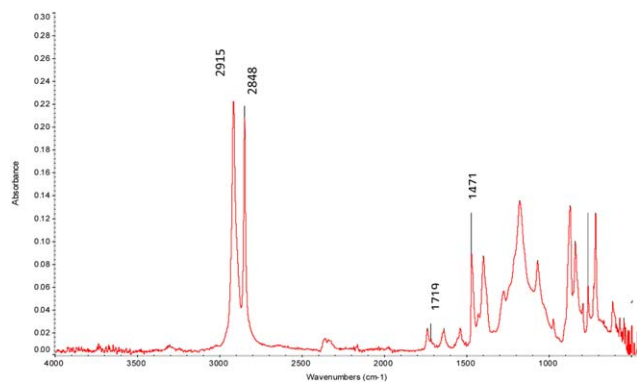


Figure 2. FTIR spectra of rHDPE. Polyethylene is the main content of the sample from the peaks at 2915 and 2848 cm^{-1} . There is also a small peak near 1719 cm^{-1} indicating that the rHDPE has gone some degradation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(extrusion, molding, etc.) in terms of exposure to shear forces, temperature, and oxygen can also accelerate degradation process of the polymers. During the end-use applications, polymers are exposed to different environments, which eventually affect polymer lifetime. Figure 3 shows the comparison of oxidation between rHDPE and vHDPE. It is clear that rHDPE used in this study has gone a little degradation compared to the vHDPE. There was no degradation of vHDPE detected in the FTIR spectra [Figure 3(a)], whereas the carbonyl index for rHDPE showed a certain amount of polymer degradation. rHDPE showed accentuated peaks [Figure 3(b)] in the range of 1740–1719 cm^{-1} (due to the carbonyl group) and another at 1640 cm^{-1} (due to double bonds),¹¹ indicating an amount of degradation. The carbonyl index values for vHDPE and rHDPE were 0 and 0.18, respectively.

Color Analysis

Visual appearances of the rHDPE and rHDPE/PCB composites before and after 2000 h of exposures to accelerated xenon-arc weathering are shown in Figures 4 and 5, respectively. Visual inspection showed that all the accelerated weathered composites

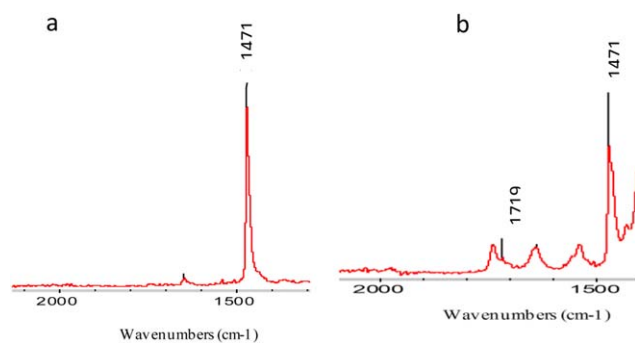


Figure 3. FTIR spectra: (a) vHDPE and (b) rHDPE. There was no degradation of vHDPE detected in the FTIR spectra [Figure 3(a)], while rHDPE showed accentuated peaks [Figure 3(b)] in the range of 1740–1719 cm^{-1} (due to the carbonyl group) and another at 1640 cm^{-1} (due to double bonds). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Figure 4. Flexural samples before weathering: (a) rHDPE, (b) 10 wt % PCB, (c) 30 wt % PCB, (d) 40 wt % PCB, and (e) 6 phr MAPE: Addition of nonmetallic PCB into rHDPE matrix turned the composite to darker color (b–d), while addition of MAPE made the color of composite lighter (e). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Figure 5. Flexural samples after 2000 h of accelerated weathering: (a) rHDPE, (b) 10 wt % PCB, (c) 30 wt % PCB, (d) 40 wt % PCB, and (e) 6 phr MAPE: All the composites tend to become lighter in color upon exposure to accelerated weathering. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

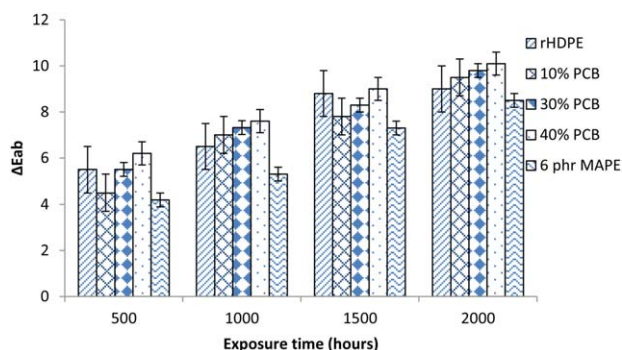


Figure 6. Differences in color changes of unfilled rHDPE, rHDPE/PCB samples with and without compatibilizer corresponding to the length of accelerated weathering. The rate of color changes for all the composites increased constantly for over 2000 h of exposure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

became lighter in color upon exposure. The surface became rough and powdery due to the matrix degradation. This was due to the high energy of UV rays which has deeply penetrated to initiate the degradation of HDPE. However, the color changes for compatibilized composites were seen less compared to samples without compatibilizer.

Figure 6 exhibits the differences of color changes (ΔE_{ab}) for each sample. It can be seen that unfilled rHDPE and rHDPE/PCB composites with and without compatibilizer suffered greatest effects from the accelerated weathering exposure. However, composite with 6 phr of compatibilizer reported reduction of 15.8% of color changes compared to composites without compatibilizer for the same formulation. Therefore, it can be supposed that the addition of MAPE compatibilizer may have contributed to the less lightening as the main role of

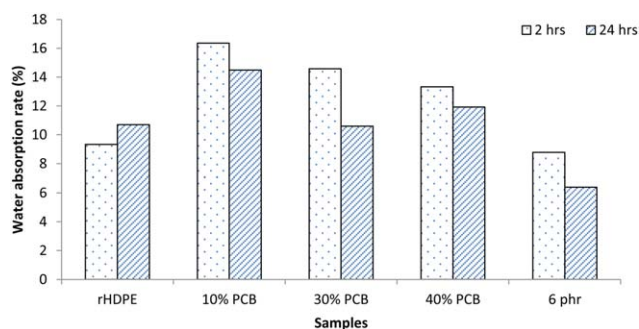


Figure 7. Water absorption rate (%) of accelerated weathered unfilled rHDPE, rHDPE/PCB composites without and with 6 phr of MAPE compatibilizer. Incorporation of MAPE compatibilizer in rHDPE/PCB composites containing 40 wt % nonmetallic PCB has played an important role in resisting degradation due to UV exposure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

compatibilizer is to improve adhesion between the incompatible phases and indirectly resulted in decreased water uptakes by the composites. It is known that water accelerates oxidation reactions and causes the fiber to swell, creating more openings for light penetration.

Water Absorption

Figure 7 shows the percentage (%) of changes in water absorption rate of weathered composites after 2 and 24 h of immersion periods.

Fracture surfaces of blends with and without MAPE compatibilizer are shown in Figure 8. Sample without compatibilizer [Figure 8(a)] showed two distinct phases. There was obvious separation between rHDPE and the nonmetallic PCB because of the incompatibility between matrix and fillers. Whereas, incorporation of 6 phr MAPE compatibilizer in rHDPE/PCB

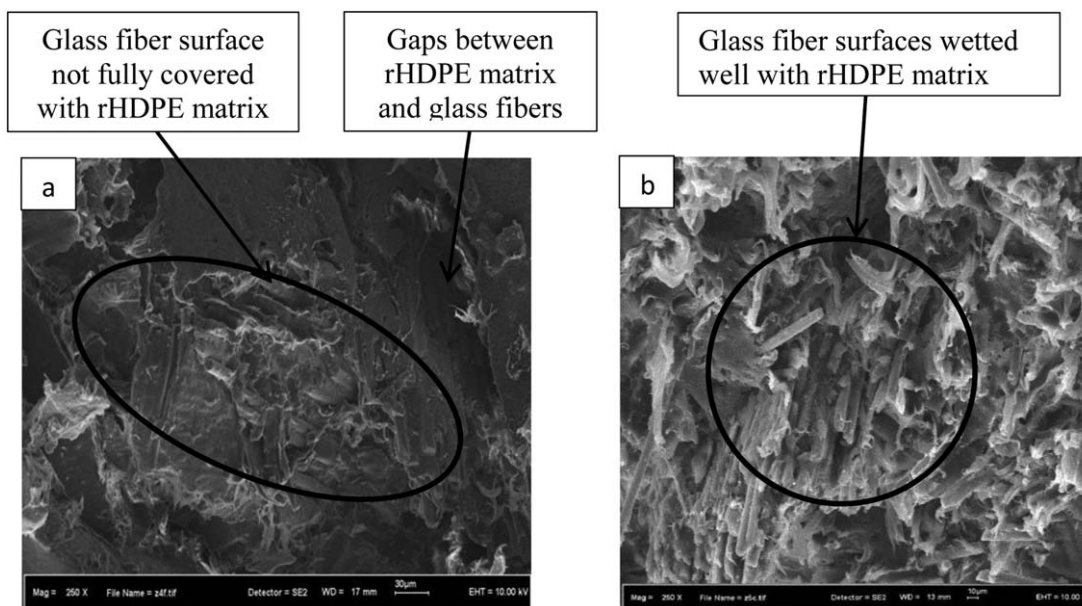


Figure 8. SEM images of the fracture surfaces of rHDPE/PCB composites with (a) 40 wt % nonmetallic PCB content and (b) 6 phr of MAPE compatibilizer.

composites had played an important role in resisting degradation due to UV exposure, as it reduced the water absorption uptakes by the composites. The main reason for the improved water absorption capability was because the number of voids and defects between the filler and polymer matrix decreased as the compatibilizer MAPE was incorporated in the composites [Figure 8(b)]. The MAPE improved the interfacial adhesion between nonmetallic PCB and polymer matrix, leading to less microvoids and fiber–polyethylene debondings, in the interface region.

Another reason for the improved resistance in compatibilized composites over composites without compatibilizer was mainly because composites with compatibilizer, the plastic penetrated into the fiber lumens, pit holes, and other void spaces in the matrix. The composite without compatibilizer showed more isolated fibers and some gaps with flaws which provided more water residence sites. The nonmetallic PCB dispersion and adhesion were slightly better in compatibilized composites when compared to composites without compatibilizer. The better dispersion might have been possible due to the improved compatibility and wettability between the rHDPE matrix and nonmetallic PCB, hence reduced the water absorptions. Moreover, presence of some impurities in the rHDPE also contributed to the higher moisture absorption at initial stage, which later deteriorated the interfacial adhesion and degraded the surface of the composites.

Photodegradation is much greater in the presence of water as the principle of water is to facilitate light penetration into previously inaccessible regions.¹² Furthermore, it has been stated that composites are subjected to a lower degree of lightening when they are exposed to only UV light, compared with exposures to a combination of UV light and water spray.¹³ Water accelerates oxidation reactions and causes the fiber to swell, creating more openings for light penetration. Additionally, water can also remove some water-soluble extractives that impart color to the filler particles.¹⁴

FTIR Analysis

After specimens were exposed in accelerated weathering condition, FTIR spectrometry was used to characterize and quantify the oxidation products present within the specimens. The photodegradation of polymers including HDPE can occur via Norrish type I and II reactions. Cross-linking and chain scission processes occurring during photo-oxidation in polyethylene are believed to be of great importance in causing changes in the mechanical properties of this material. Photodegradation via Norrish type II leads to polymer chain scission and formation of carbonyl group, which is considered as one of the groups that can be detected during the FTIR spectroscopy process to indicate the oxidation rate.

Figure 9 shows the FTIR spectra of unfilled rHDPE and rHDPE/PCB composites with and without compatibilizer before and after 2000 h of accelerated weathering. It can be noted that there is an increase in the intensities of the absorption bands associated with carbonyl at 1718 cm^{-1} after weathering exposure indicating the occurrence of photo-oxidation in all the samples.

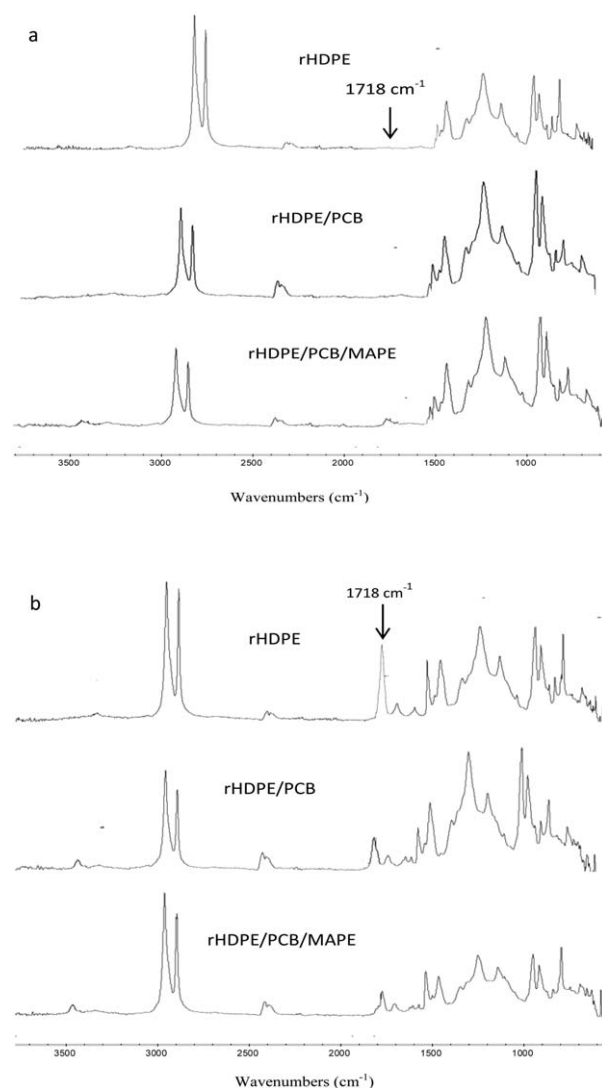


Figure 9. FTIR spectra of unfilled rHDPE, rHDPE/PCB composites with and with 6 phr MAPE compatibilizer (a) before and (b) after 2000 h of accelerated weathering. There is an increase in the intensities of the absorption bands associated with carbonyl at 1718 cm^{-1} after weathering exposure indicating the occurrence of photo-oxidation in all the samples.

Figure 10 shows the carbonyl index (CI) of the unfilled rHDPE and rHDPE/PCB samples with and without compatibilizer due to accelerated weathering, respectively. These data were processed from FTIR-ATR spectra. For all the samples, the CI increases with exposure time indicating that the oxidation reaction continuously occurred during the aging process. Interestingly, rHDPE matrix filled with nonmetallic PCB materials seemed to be more stable than unfilled rHDPE samples. Moreover, rHDPE/PCB composites compatibilized with MAPE had shown some reduction in CI to some extent compared to composites without compatibilizer.

The observed reduction in CI in compatibilized composites with incorporation of MAPE compatibilizer was mainly because the voids were filled by small particles of adhesive and coatings which hindered the rate of absorption of water. This confirms that the compatibilizer aided in protecting against chain

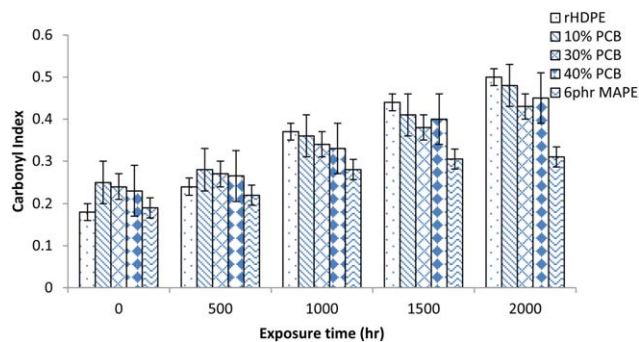


Figure 10. Carbonyl Index of accelerated weathered unfilled rHDPE and rHDPE/PCB composites with 10%, 30%, 40% nonmetallic PCB and 6 phr of MAPE compatibilizer. For all the samples, the CI increases with exposure time indicating that the oxidation reaction continuously occurred during the aging process. rHDPE/PCB composites compatibilized with MAPE have shown some reduction in CI to some extent compared to composites without compatibilizer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

scission. Indeed, the CI did not significantly increase for the compatibilized composites regardless of duration of weathering.

Flexural Properties

The samples were also tested for their flexural properties after being exposed for duration of 2000 h of accelerated weathering. Generally, no significant changes were reported for all the flexural strength values for the first 500 h of exposure. However, at 1000 h, the flexural strength values were started to drop with continuous exposure up to 2000 h.

It can be observed from Figure 11, after 2000 h of exposure, the flexural strength of unfilled rHDPE matrix dropped by about 42.2% while rHDPE/PCB composites filled with 10, 30, and 40 wt % nonmetallic PCB lost their flexural strength values by about 36.6%, 32.8%, and 28.2%, respectively. Interestingly, flexural strength values of all the accelerated weathered rHDPE/PCB composites with nonmetallic PCB were significantly greater than those of unfilled rHDPE matrix, regardless of the length of exposure.

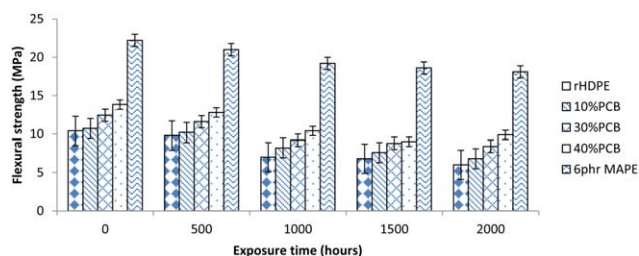


Figure 11. Flexural strength of accelerated weathered unfilled rHDPE and rHDPE/PCB composites with 10%, 30%, 40% nonmetallic PCB and 6 phr of MAPE compatibilizer. Flexural strength of all the accelerated weathered rHDPE/PCB composites with nonmetallic PCB was significantly greater than those of unfilled rHDPE matrix, regardless of the length of exposure. MAPE-compatibilized composites exhibited less decrease in the flexural strength. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

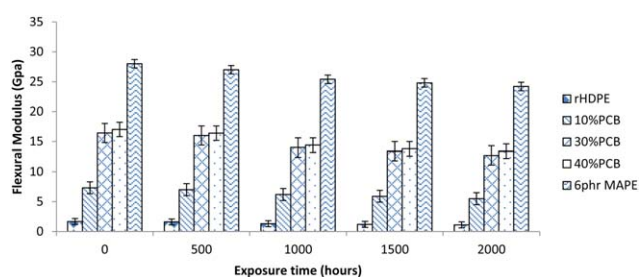


Figure 12. Flexural modulus of accelerated weathered unfilled rHDPE and rHDPE/PCB composites with 10%, 30%, 40% nonmetallic PCB and 6 phr of MAPE compatibilizer. After 2000 h of accelerated weathering exposure, the rHDPE/PCB composites with 40 wt % nonmetallic PCB had the greatest flexural properties and unfilled rHDPE matrix with the lowest flexural properties of all formulations. Reduction in strength and modulus were less for the composites with MAPE addition after weathering compared to composites without compatibilizer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

MAPE-compatibilized composite exhibited less decreases in the flexural strength value when compared to composites without MAPE. For example, for composites with 40 wt % nonmetallic PCB content, the flexural strength value was reduced by 18.3% with addition of 6 phr of MAPE compatibilizer, respectively, compared to reduction of 28.2% without compatibilizer.

Flexural modulus values (Figure 12) of the weathered samples also exhibited almost the same trend as flexural strength. Flexural modulus of unfilled rHDPE dropped by about 32.6%, while, flexural modulus values of rHDPE/PCB composites with 10, 30, and 40 wt % nonmetallic PCB dropped by about 24.6%, 22.8%, and 21.2%, respectively. However, with the incorporation of MAPE compatibilizer at loading of 6 phr, the flexural modulus value reduced by only 13.5% compared to 21.2% reduction without compatibilizer.

Overall, after 2000 h of accelerated weathering exposure, the rHDPE/PCB composites with 40 wt % nonmetallic PCB had the greatest flexural properties and unfilled rHDPE matrix with the lowest flexural properties of all formulations. The deteriorating effect of weathering on flexural strength was much less with the presence of nonmetallic PCB particles possibly because glass fibers contained in the nonmetallic PCB materials protected the rHDPE matrix from being exposed to UV radiation. This could be one the reasons for the improved flexural properties of composites filled with nonmetallic PCB.

In addition, the reduction in strength and modulus was less for the composites with MAPE addition after weathering compared to composites without compatibilizer. This is mainly because of the modified interface bonding in the presence of the MAPE. Penetration of water into the composites through the interface was restricted, which could be the reason for the improved flexural properties with weathering.

SEM observations have revealed that, in general, all the unweathered composite samples showed considerable amount of fibers and matrix breakage with limited intact materials on the surfaces of the samples. However, weathered samples showed decreased bonding between matrix and fibers as reflected by the

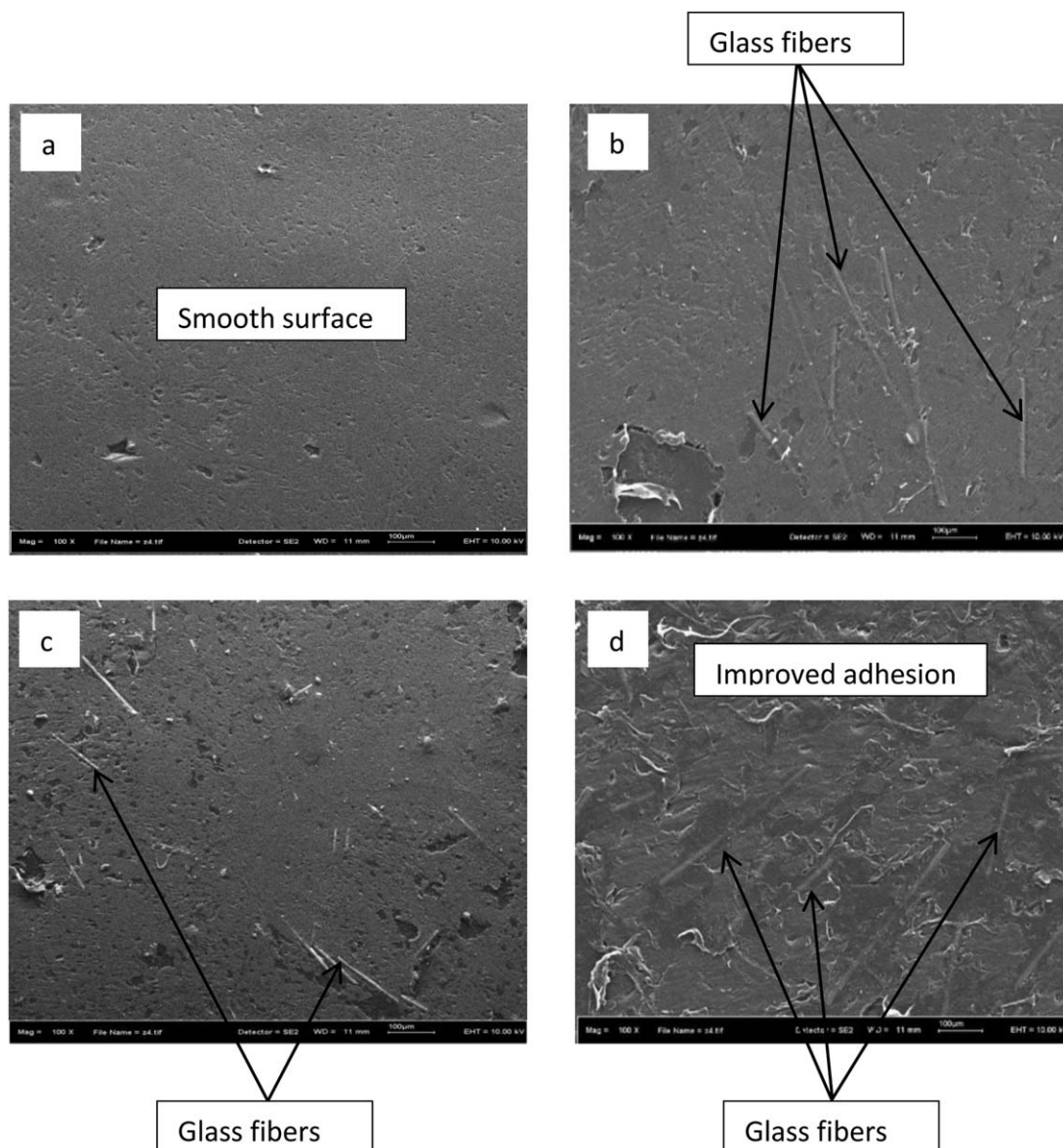


Figure 13. SEM images of (a) unfilled rHDPE and rHDPE/PCB composites with (b) 30 wt % PCB, (c) 40 wt % PCB, and (d) 40 wt % PCB with 6 phr MAPE compatibilizer before weathering.

numbers of glass fibers being pulled out from rHDPE matrix. These phenomena were valid for all composite formulations irrespective of filler content and the use of compatibilizer. These could also be used to explain the reduction in the mechanical properties of the composites after weathering.

For unweathered sample of rHDPE [Figure 13(a)], prior to the weathering test, the surface of the sample was smooth. Little degradation was observed on the surface with continued weathering until 1000 h [Figure 14(a)]. However, after 2000 h of exposure [Figure 15(a)], oxidation process took place vigorously leading to severe surface degradation.

For rHDPE/PCB composites with 30 wt % [Figure 13(b)] and 40 wt % [Figure 13(c)] of nonmetallic PCB prior to weathering, it was noted that glass fibers from the nonmetallic PCB materi-

als were found randomly on the surfaces. The unweathered samples also exhibited a considerable amount of matrix and fiber fracture, leaving a relatively smooth fracture surfaces. This indicated good interface bonding between the nonmetallic PCB fibers and polymer matrix. Furthermore, it was observed that glass fibers almost covered the whole surface of specimens, acting as a protective layer. It can thus prevent exposure of the polymer surfaces to direct UV irradiation, slowing down the photodegradation reactions.

Moreover, after 1000 h of accelerated weathering for rHDPE/PCB composites with 30 wt % nonmetallic PCB [Figure 14(b)] and 40 wt % nonmetallic PCB [Figure 14(c)], nonmetallic particles became more apparent and protruded out of the composite surfaces when the rHDPE matrix covering the particles had

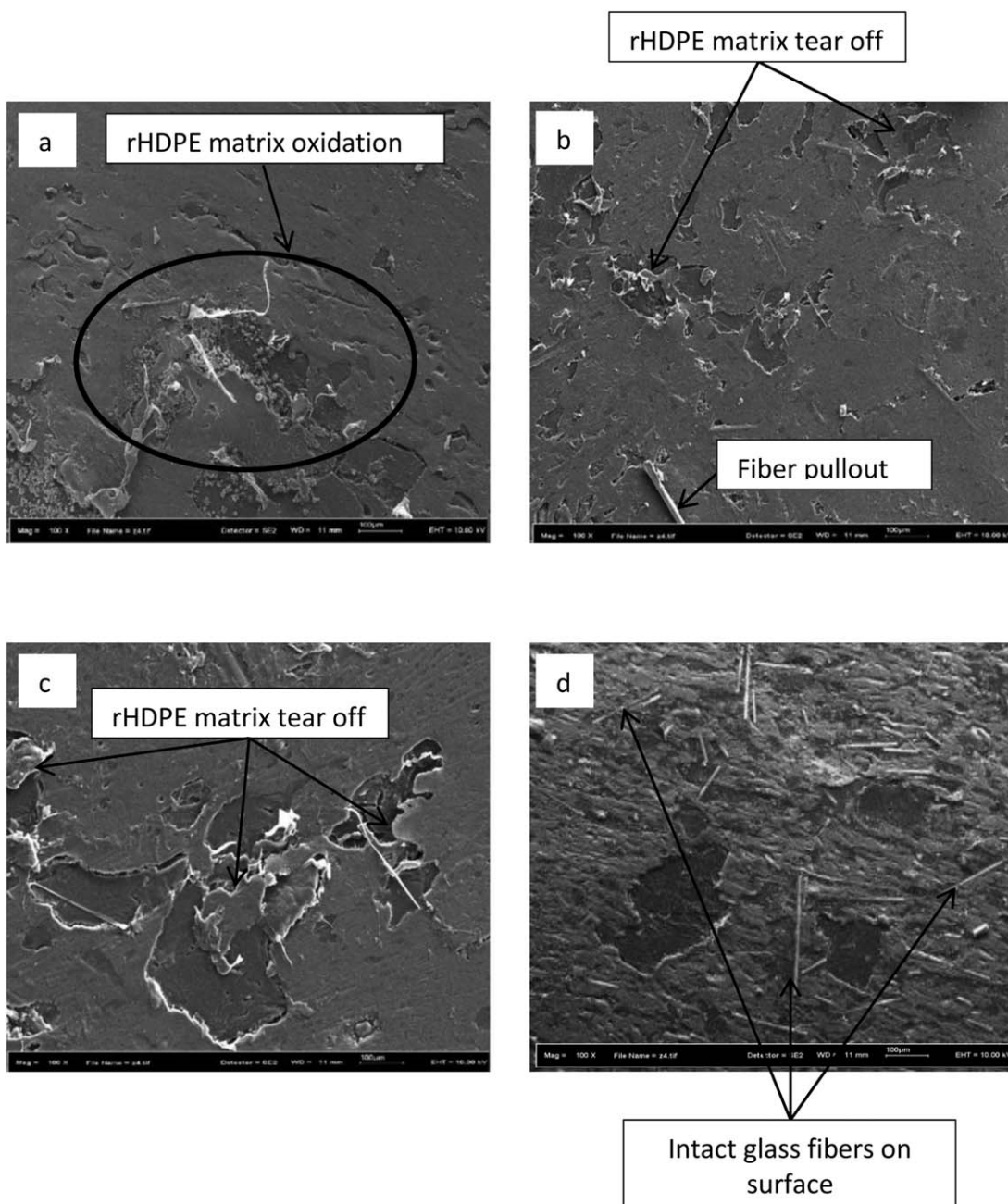


Figure 14. SEM images of (a) unfilled rHDPE and rHDPE/PCB composites with (b) 30 wt % PCB, (c) 40 wt % PCB and (d) 40 wt % PCB with 6 phr MAPE compatibilizer after 1000 h of accelerated weathering.

broken into small pieces and fallen out. Apart from that, the adsorption and desorption of moistures also promoted void formation and initiated cracks. As the exposure periods prolonged, cracks started to propagate and eventually deteriorated the interfacial properties of matrix and fiber. Thus, the surfaces of the rHDPE composites apparently began to flake after 2000 h [Figure 15(b,c)].

Meanwhile, Figure 13(d) illustrates the surface of the 6 phr MAPE-compatible composite prior to weathering exposures. From the image, it can be seen that the rHDPE/PCB composite with MAPE showed smoother surface with less evidence of

voids compared to composites without MAPE. The nonmetallic PCB filler materials were well coated in the matrix and the presence of MAPE improved the interfacial adhesion between the filler and matrix.

With continuous exposures to weathering, the compatibilized composite surface experienced degradation too. For the first 1000 h of accelerated weathering [Figure 14(d)], the compatibilized composite surface was seen not much affected with little intact materials on the surface. With continuous weathering up to 2000 h [Figure 15(d)], the surface was seen fractured with apparent fine cracks. However, the cracks were not as deep as

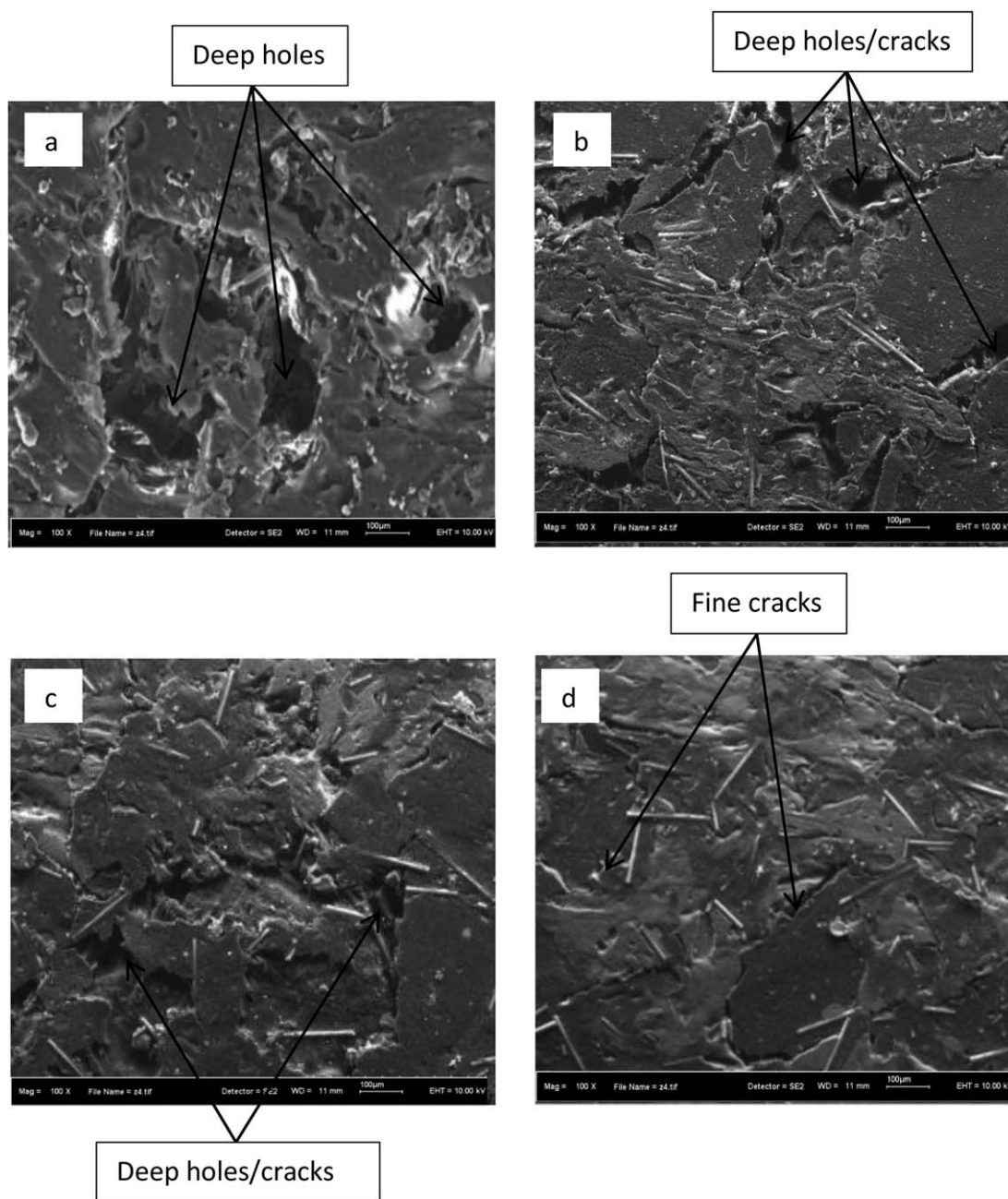


Figure 15. SEM images of (a) unfilled rHDPE and rHDPE/PCB composites with (b) 30 wt % PCB, (c) 40 wt % PCB and (d) 40 wt % PCB with 6 phr MAPE compatibilizer after 2000 h of accelerated weathering.

seen in composites without compatibilizer, indicating an improved resistance to weathering for the compatibilized samples.

Crystallinity Changes

Crystallinity increases are an indication of chain scission as the smaller molecules undergo recrystallization. Generally, with the addition of nonmetallic PCB to the rHDPE matrix hinders the ability of rHDPE to crystallize. As a result, the percentages of crystallinity before weathering are lower for the composites with nonmetallic PCB than for the unfilled rHDPE matrix (Table III). For all the composites, the crystallinity increased

upon 2000 h of weathering. This indicates that chain scission may have occurred throughout the exposures and surfaces oxidations for all the composites increased with exposure periods. The shorter chains produced during chain scission are more mobile and are able to crystallize more readily, which resulted in increased crystallization and associated embrittlement which then deteriorated the mechanical properties of the composites upon weathering exposure.

Considerable changes in crystallinity were observed only at the time of rapid growth of carbonyl index where chain scission occurs. Increase in carbonyl group formation for composites

Table III. %Xc Data of rHDPE/PCB Composites with and without Compatibilizer

Composite sample	%Xc	
	Before weathering	After 2000 h of weathering
rHDPE	42.2	49.4
rHDPE/PCB (90/10)	33.1	36.5
rHDPE/PCB (70/30)	32.3	36.0
rHDPE/PCB (60/40)	30.4	33.2
rHDPE/PCB (60/40) with 6 phr MAPE	31.2	31.8
rHDPE/PCB (60/40) with 12 phr MAPE	31.5	31.9
rHDPE/PCB (60/40) with 18 phr MAPE	32.0	33.0

Percentage crystallinity before weathering is lower for the composites with nonmetallic PCB than for the unfilled rHDPE matrix. For all the composites, the crystallinity increased upon 2000 h of weathering.

after weathering is known to be proportional to the number of chain scissions occurring in polymer matrix.¹⁵ Addition of compatibilizer effectively delayed some degradation properties of weathering; it prevents a significant loss in crystallinity, which in turn delays the appearances of surface cracking and consequent loss in mechanical properties.

Toxicity Characteristic Leaching Procedure (TCLP) Test after Weathering Exposure

In this study, TCLP testing was conducted to analyse the heavy metal contaminations in rHDPE/PCB composites with and without compatibilizer before and after accelerated weathering exposure. Testing was done in three replicates and the average value was reported. The rHDPE/PCB composites with maximum content of the nonmetallic PCB (40 wt %) and with addition of 6 phr of MAPE compatibilizer were selected to study the leaching characteristics before and after 2000 h of accelerated weathering exposure (Table IV).

The concentrations of Cu leached from all the composite materials before and after weathering test were far below the regulatory limits which are only around 3 mg/L. The concentration of

Cu was the highest among all the other metal ions in leachate mainly due to the highest residual Cu particles in the nonmetallic PCB waste compared to other metals. Cu particles in the nonmetallic PCB waste were encapsulated by resin powder and glass fibers, making it difficult and hard to separate the Cu particles from the nonmetallic materials completely.^{1,2} While, for other metallic constituents as listed in Table II, all the ion concentrations were far below the regulatory limits and identification standards for hazardous waste regardless of duration of weathering exposure. Therefore, it can be concluded that composites made from nonmetallic PCB materials are safe to be used in making practical products for outdoor applications as they do not pose threat to human and surrounding environment.

CONCLUSION

All the samples weathered up to 2000 h in xenon-arc chamber became lighter in color upon exposure. Weathered composites with addition of 6 phr MAPE compatibilizer showed the lowest color changes compared to all the composites without compatibilizer. It was noted that the presence of compatibilizer had

Table IV. Leaching Test of rHDPE/PCB Composites with and without Compatibilizer before and after Accelerated Weathering

Metals	Units	LOR	STD ^a	Before		After weathering (2000 hrs)	
				Without compatibilizer	With compatibilizer	Without compatibilizer	With compatibilizer
Arsenic	mg/L	0.05	5	<0.05	<0.05	<0.05	<0.05
Barium	mg/L	0.1	100	<0.1	<0.1	<0.1	<0.1
Cadmium	mg/L	0.01	1	<0.01	<0.01	<0.01	<0.01
Chromium	mg/L	0.01	5	<0.01	<0.01	<0.01	<0.01
Lead	mg/L	0.05	5	<0.05	<0.05	<0.05	<0.05
Mercury	mg/L	0.001	0.2	<0.001	<0.001	<0.001	<0.001
Selenium	mg/L	0.1	1	<0.1	<0.1	<0.1	<0.1
Silver	mg/L	0.01	5	<0.01	<0.01	<0.01	<0.01
Copper	mg/L	0.1	100	3.00	2.22	2.90	2.20

LOR: level of reporting; USEPA: United States Environmental Protection Agency.

^aMaximum concentration of contaminants for the toxicity characteristics leaching procedure (TCLP).

All the ion concentrations were far below the regulatory limits and identification standards for hazardous waste regardless of duration of weathering exposure.

played an important role in resisting degradation due to UV exposures as it has the lowest water absorption rate compared to all the other composites without compatibilizer. The mechanical properties of unfilled rHDPE and rHDPE/PCB composites filled with 10, 30, and 40 wt % nonmetallic PCB were found to decrease throughout the 2000 h of exposure. However, with incorporation of MAPE compatibilizer at loadings of 6, 12 and 18 phr, the mechanical properties decreased lesser compared to composites without compatibilizer. For all the weathered samples, the carbonyl index increases with exposure periods indicating that the oxidation reactions continuously occurred during the aging process.

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