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Natural Weathering of Kenaf Bast Fibre-Filled Poly(Butylene Succinate) Composites: Effect of Fibre Loading and Compatibiliser Addition

M. Z. Ahmad Thirmizir · Z. A. Mohd Ishak · R. Mat Taib · S. Rahim · S. Mohamad Jani

Abstract Natural weathering was performed on poly(butylene succinate) (PBS) and its kenaf bast fibre (KBF) filled composites by exposing the specimens to a tropical climate for a period of 6 months (max–min temperature: 31.5–23.9 °C; relative humidity: 78.9%). The aim of this study was to investigate the effects of KBF loading and the addition of maleated PBS compatibiliser (PBSgMA) on the performance of the composites under natural weathering. As expected, the flexural properties of both the uncompatibilised and compatibilised composites dropped with increasing exposure time. The weathered specimens were also assessed by colour change analysis, FTIR spectroscopy analysis and SEM examination. The total colour change, ΔE_{ab}, of both the uncompatibilised and compatibilised composites increased with weathering time. FTIR spectroscopy analysis confirmed the presence of oxidation products such as hydroxyl, carbonyl and vinyl species in the weathered uncompatibilised and compatibilised composites. SEM examination revealed the presence of surface defects such as cracking, tiny holes and degraded fibre, which explain the poor performance of the composites upon weathering.

Keywords Mechanical properties · Natural fibre-plastic composites · Natural weathering · Compatibiliser

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Introduction

Natural fibre-plastic composites (NFPCs) have been widely used in the automobile, construction and packaging industries over the past decade due to the advantages of natural fibres including their relatively high strength and stiffness, low density, renewable resource, and naturally biodegradable [1]. The outdoor applications of these products raise concerns in terms of their durability, including UV resistance, fungal resistance, moisture resistance and dimensional stability [2]. The natural weathering test is an essential way to investigate the durability of the composites in their service life [3]. Because Malaysia experiences a hot and wet tropical climate, it represents an interesting environment in which to investigate the ability of the PBS/KBF composites to withstand the extreme environmental degradation. In this study, PBS was chosen as the composite matrix due to its outstanding mechanical properties compared to PE and its biodegradability when disposed in the natural environment [4]. KBF was incorporated in this composite to reduce the material cost and to produce a fully-biodegradable material.

Both polymer matrix and natural fibre in NFPCs will experience solar degradation during natural weathering. Photodegradation upon ultraviolet (UV) exposure is expected to be the major cause of changes to the surface appearance and chemistry of the composite products that usually lead to discoloration and a loss in structural integrity [1]. During weathering, the polymer matrix may degrade via Norrish Type I and II chain scission reactions [5]. However, for carbonyl containing polymers, the presence of a chromophoric group (C=O) will enhance the absorption of solar UV radiation [6]. According to Yew et al. [7], the absorption of short wavelength UV radiation

could break the C–C, C–N, O–O, C–Cl, C–O, N–H, and Si–O types of polymer bonds, thus damaging the polymeric materials. Tertiary hydrogens belonging to CH_3 groups in the polymer backbone will also be degraded by photooxidation reactions during natural weathering [7]. According to Muasher and Sain [1], photooxidation reactions that occur via Norrish Type I reactions will result in the formation of free radicals and may lead to a termination via cross linking or chain scission. However, Norrish Type II reactions will result in the formation of both carbonyl and vinyl groups. This formation will cause the polymer to become brittle and will decrease properties such as melt flow/viscosity, molecular weight, and mechanical strength upon exposure [5]. Additionally, the presence of moisture in the environment will hydrolyse the ester linkages, thus facilitating polymer degradation [5].

The photodegradation of natural fibre is attributed to the degradation of its components, namely cellulose, hemicellulose, lignin and extractives, and can usually be detected by an initial colour change, followed by a loss of gloss, roughening and checking [8]. In addition, discolouration of lignocelluloses upon exposure to sunlight is attributed to the modification of the chromophoric functional groups (i.e., carboxylic acids, quinones and hydroperoxy radicals) [1]. The result of photodegradation is the formation of ortho-and para-quinone structures with a characteristic yellow colour [8, 9]. NFPCs are prepared with compatibiliser to improve the fibre-matrix interfacial adhesion between hydrophobic polymers and hydrophilic fibres. Previously, several studies have reported an outstanding improvement in fibre-matrix interfacial adhesion, and an enhancement in the composite strength was achieved with the addition of PBSgMA to PBS matrix composites [4, 10]. Thus far, there are not many studies examining the effect of compatibiliser on the durability of the NFPCs upon natural weathering. There appears to be no study reporting on the durability of PBS/KBF composites compatibilised with PBSgMA upon exposure to hot and wet tropical climate, so it is interesting to investigate the durability of these compatibilised composites under natural weathering. In general, this study characterises the durability of composites upon natural weathering by changes in chemical, physical and mechanical properties.

Experimental

Materials

Water retted kenaf bast fibre (KBF) in final lengths ranging from 0.8 to 1.0 mm and diameters ranging of 70–90 μm was supplied by Kenaf Fibre Industries Sdn. Bhd. (KFI), Malaysia. Poly(butylene succinate) (PBS) with the trade name Bionolle with a melt flow index of 28 g/10 min and a density of 1.25 g/cm^3 was supplied by Showa Highpolymer, Japan. Maleic anhydride (MA) (99%, R&M Chemical), dicumyl peroxide (DCP) (98%, Sigma–Aldrich) and chloroform (Merck) were used as received.

Preparation of PBSgMA Compatibiliser

Reactive mixing of PBSgMA was conducted using a Brabender internal compounder with co-rotating double winged rotors at 140 °C with a 50 rpm rotor speed for a period of 5 min. Prior to being fed into the compounding chamber, PBS, DCP and MA were premixed thoroughly in a plastic container. Four different formulations of compatibiliser were tested as shown in Table 1. The reactively mixed compatibilisers were purified by refluxing in chloroform for 1 h. The reflux solution was poured into cool methanol and filtered. The precipitated polymer was then further washed with fresh methanol to remove residual unreacted MA and DCP. Finally, the polymer was dried in a circulating air oven at 80 °C for 24 h and kept in a sealed plastic bag prior to use.

Determination of Grafting Degree

The anhydride content of grafted polymer was determined by titration of acid groups derived from anhydride functional groups through the method proposed by Mani et al. [11], amended according to the suggestion of Zhu and Tang [12]. This method involved dissolution of 1 g purified PBSgMA compatibilisers in 100 mL refluxing chloroform for 30 min. Then, 5 mL of distilled water were added to the hot solution to hydrolyse the anhydride groups. The hot solution was titrated immediately against 0.025 N ethanolic KOH in the presence of 4 drops of 1% phenolphthalein in ethanol as an indicator. Titration was stopped once the purple end point indication was reached. A blank titration was also carried out in the same way to the compatibiliser titrations. The grafting degree of MA to PBS was calculated using Eq. 1.

Table 1 Formulation of PBSgMA compatibiliser

PBSgMA	Parts per hundred (phr)			Grafting degree (%)
	PBS	MA	DCP	
3PBSgMA	100	3	1	0.91 ± 0.03
5PBSgMA	100	5	1	1.07 ± 0.02
7PBSgMA	100	7	1	2.14 ± 0.04
10PBSgMA	100	10	1	2.32 ± 0.05

$$\text{Grafting degree of MA} = \frac{98.06 \times c \times (V - V_o)}{2 \times 1000 \times m} \times 100\% \tag{1}$$

where V and V_o (mL) represent the volume of the KOH/C_2H_5OH solution used for titration of the grafted and blank samples, C (mol/L) is the molar concentration of the KOH/C_2H_3OH solutions, 98.06 (g/mol) is the molecular weight of MA, m (g) is the weight of the grafted sample, and 2 indicates that one anhydride group could change to two carboxylic groups after opening the rings of the MA.

Composite Compounding and Specimen Preparation

For uncompatibilised composites, four different KBF loadings were tested (10, 20, 30 and 40 wt%). For compatibilised composites, the fibre, compatibiliser and polymer loadings were fixed at 30, 5 and 65 wt%, respectively. The composites were compounded using a Brabender internal mixer with co-rotating double winged rotors. The processing temperature was set at 130 °C. For composites containing PBSgMA, PBS and the compatibiliser were physically premixed in a plastic container before feeding them into the mixing chamber. Then, the fibre was added gradually into the chamber under a low rotor speed (10 rpm). After that, the compounding process was continued at 50 rpm rotor speed for 5 min before discharge. The composite compounds were compression moulded at 130 °C into specimens with dimensions of $120 \times 12 \times 3$ mm^3 using a compression moulding machine (model Kao Tieh Gotech). The moulding cycle involved 5 min of preheating without pressure, 3 min of compression under 150 kg/cm^3 of pressure and 5 min of cooling under the same pressure. Prior to testing, the moulded specimens were kept in desiccators and conditioned at room temperature for at least 24 h.

Natural Weathering

The natural weathering test was carried out according to ASTM D 1435. Specimens with dimensions of $120 \times 12 \times 3$ mm^3 were attached to a stainless steel rack

Table 2 Weathering conditions during the exposure of specimens to natural weathering from January to June 2009

Exposure (month)	Temperature (°C)		Relative humidity (%)	Rainfall (mm)
	Maximum	Minimum		
January 2009	31.2	22.6	72.0	257.6
February 2009	31.4	23.0	75.6	128.4
March 2009	31.5	23.8	80.7	194.5
April 2009	31.8	24.4	80.6	530.7
May 2009	31.3	24.5	80.8	473.5
June 2009	32.6	24.6	75.9	179.9

equipped with specimen holders. The rack was set to face the equator at 45° and was exposed at the weathering site of the School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia. Weather reports for the 6 month exposure period were obtained from the Meteorological Department of Penang State, Malaysia and are summarised in Table 2. The specimens were collected every 2 months for a total 6 months period of exposure, and were assessed using flexural tests, FTIR spectroscopy analysis, colour change analysis and SEM surface morphology examination. Prior to analysis, all specimens were dried at 70 °C for 24 h to remove any moisture.

Flexural Properties

Flexural testing was carried out on the unweathered and weathered composites every 2 months for a total of 6 months exposure. The test was carried out in accordance with ASTM D 790-98 using a universal testing machine (UTM) model Instron 3366 equipped with control system series IX. The crosshead speed was set at 5 mm/min. 5 specimens were tested for each sample type.

Colour Change Measurement

Colour measurements of the surfaces of unweathered and weathered specimens were recorded using a spectrometer model Konica Minolta Chroma Meter CR-400. Prior to measurement, the specimens were cleaned and conditioned at room temperature for 24 h. Colour is expressed using the CIELAB system, which consists of (L^*, a^*, b^*) colour coordinates based on a D65 light source. Lightness (L) and chromacity coordinates (a) and (b) were measured for 3 replicates. The total change in colour (ΔE_{ab}) was calculated using the Euclidean distance expressed in Eq. 2:

$$\Delta E_{ab} = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \tag{2}$$

where ΔL, Δa, and Δb represent the differences between the initial and final values of L^*, a^*, and b^*, respectively. An increase in the L value means the specimen is fading (i.e., a positive ΔL indicates lightening and a negative ΔL indicates darkening. The a^* coordinate represents the red-green direction, while the b^* coordinate represents the yellow-blue direction. A positive Δa signifies a colour shift towards red and a negative Δa signifies a colour shift towards green, while a positive Δb signifies a colour shift towards yellow and a negative Δb signifies a shift towards blue.

FTIR Spectroscopy Analysis

FTIR spectra were measured directly on the surface of unweathered and 2, 4 and 6 months weathered specimens

using a FTIR spectrometer model Perkin Elmer System 2000. The FTIR spectra were obtained using attenuated total reflectance (ATR) within the band range of 600–4,000 cm^{-1} and recorded in absorbance unit. The scans were run at a resolution of 4 cm^{-1} and 32 scans were taken for each spectrum. The ATR correction was carried out before analyze the spectra. The peaks were analyzed after smoothen the spectra. Hydroxyl, carbonyl and vinyl indexes were calculated using the Eqs. 3, 4 and 5, respectively:

$$\text{Hydroxyl Index (HI)} = \frac{I_{3200-3600}}{I_{2920}} \quad (3)$$

$$\text{Carbonyl Index (CI)} = \frac{I_{1711}}{I_{2920}} \quad (4)$$

$$\text{Vinyl Index (VI)} = \frac{I_{916}}{I_{2920}} \quad (5)$$

where I represents the peak intensity. According to Stark and Matuana [13] the peak corresponds to alkane C–H stretching vibrations of the methylene groups normally chosen as the reference peak. In this study the peak at 2920 cm^{-1} was chosen as the reference peak because it changed the least during weathering of PBS.

Surface Observation

Morphological study of the unweathered and weathered surfaces was carried out by taking scanning electron micrographs at an acceleration voltage of 25 kV and pre-determined magnifications using a low vacuum mode scanning electron microscope (model FEI Quanta 200). The specimens were observed as prepared. The morphological study of the weathered surface was carried out to observe the deteriorating impact of natural weathering on the specimens.

Results and Discussion

Effect of Natural Weathering on Flexural Properties

Effect of Fibre Loading

Figure 1 shows the effect of exposure time on the flexural strength of PBS and PBS/KBF composites. Generally, increasing the KBF loading from 10 to 30 wt% resulted in increases in the flexural strength of the unweathered composites of 12–24%, while at 40 wt% KBF loading, a reduction in flexural strength of about 13.4% was observed. However, for the weathered composites (2, 4 and 6 months exposure), the flexural strength of the composites decreased with increasing fibre loading. This result
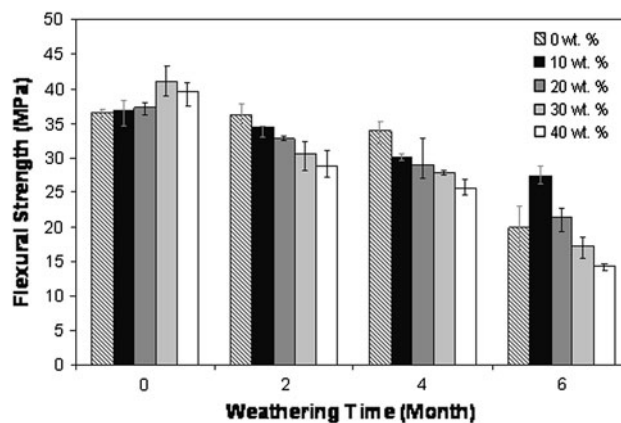

Fig. 1 Effect of natural weathering on the flexural strength of PBS/KBF composites with different fibre loadings

indicates that the reinforcing effect of the KBF has deteriorated upon natural weathering. In all cases, the flexural strength of the composites decreased with increasing weathering time, most likely due to degradation of the composite constituents during exposure due to thermo-oxidation, photo-oxidation and chain scission reactions [14].

Figure 1 indicates that the flexural strength of the weathered PBS also decreased with increasing weathering time, probably due to photo-oxidation of the polymer itself. According to Abu-Sharkh and Hamid [14], exposure of polymers to UV rays during natural weathering will results in chain scission of the polymers. The C=O group in the PBS likely absorbed the UV rays during exposure, thus resulting in the cleavage of the C–O ester and the C–C bonds of the polymer main chain. This result is also in line with findings by Yew et al. [7] in their study on natural weathering of PLA. As a consequence the properties of the polymer including melt flow/viscosity, molecular weight, and mechanical strength have deteriorated [12]. Exposure to UV rays during natural weathering also leads to rapid degradation of fibre constituents such as lignin, hemicelluloses, and cellulose [15]. According to Chang and Chang [16], absorption of incident UV light by lignocellulosic components during natural weathering will result in photo-chemical and photo-physical degradation of the lignocellulosic components (especially lignin). Photo-chemical degradation will act in combination with moisture, temperature, and oxidative agents such as oxygen and/or ozone to depolymerise lignin and cellulose components, thus leading to a reduction in some physical, chemical and biological properties of the lignocellulosic material [8].

The presence of moisture (i.e., air, rain and dew) during natural weathering could also accelerate the degradation of the composites [6, 17]. Moisture could absorb into lignocelluloses/polymer composites through capillary action of

fibre-matrix interfacial gaps, fibre absorption and diffusion through polymer chains [18]. The absorbed moisture could deteriorate the fibre properties and fibre-matrix interfacial adhesion. Furthermore, the deterioration of the integrity of the composite structure is also accelerated by the cyclic expansion and contraction of the specimens resulting from fluctuating climatic conditions [17].

Figure 2 shows the effect of natural weathering on the flexural modulus of PBS and PBS/KBF composites with fibre loadings of 10, 20, 30 and 40 wt%. In general, the flexural moduli of the weathered specimens were lower than those of unweathered specimens. This finding is common for lignocellulosic-polymer composites where exposure to photo-oxidation and thermo-oxidation reactions during natural weathering results in a more brittle composite [14]. The flexural moduli of the unweathered composites seem to increase with increasing fibre loading. However, after exposed to natural weathering, the flexural modulus of the composites only increased with increasing fibre loading from 10 to 30 wt% before decreasing at a fibre loading of 40 wt%. According to the flexural strength results of the unweathered composites, the optimum increment was achieved at a fibre loading of 30 wt%. Perhaps the incorporation of KBF in excess of the optimum fibre loading leads to poor fibre wetting by the polymer matrix, thus making the flexural modulus inferior once it is exposed to natural weathering. As seen in Fig. 2, all the composites besides that with 40 wt% fibre loading show good retention of flexural modulus at 2 and 4 months of exposure before decrease at 6 months of exposure. In the case of the composite with 40 wt% KBF loading, the reduction in flexural modulus was observed as early as 4 months exposure. This probably due to the greater number of fibre–fibre interactions at incorporation of KBF in excess of the optimum loading and an increase in PBS brittleness resulting from polymer chain scission.
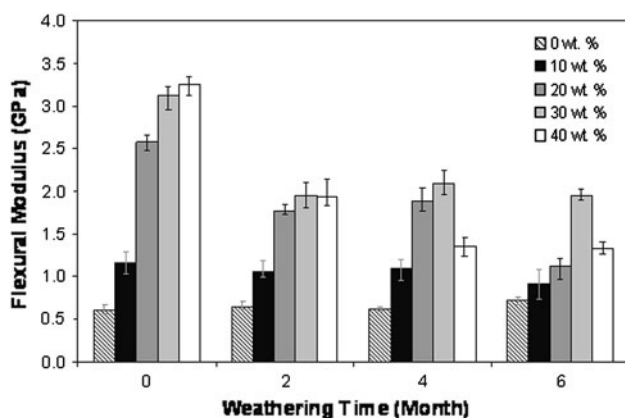
Effect of Compatibiliser Addition

Figure 3 shows the effect of compatibiliser on the flexural strength of the PBS30KBF composites weathered for 6 months. Generally, the flexural strength of the compatibilised composites declined with increasing weathering time. The decrease in flexural strength was probably due to photo-oxidation and chemical-oxidation of the composite components during natural weathering [14]. These degradations tend to reduce the molecular weight of the polymer matrix, break down the fibre constituent integrity and deteriorate the fibre-matrix interfacial adhesion [1, 14, 15]. The flexural strength of the compatibilised composites weathered for 2, 4 and 6 months decreased with increasing MA concentration of the compatibilisers. This result shows that the increase in MA concentration had a detrimental effect on the strength of the weathered composites.

According to Abu-Sharkh and Hamid [14], compatibilised composites are less stable than uncompatibilised ones.
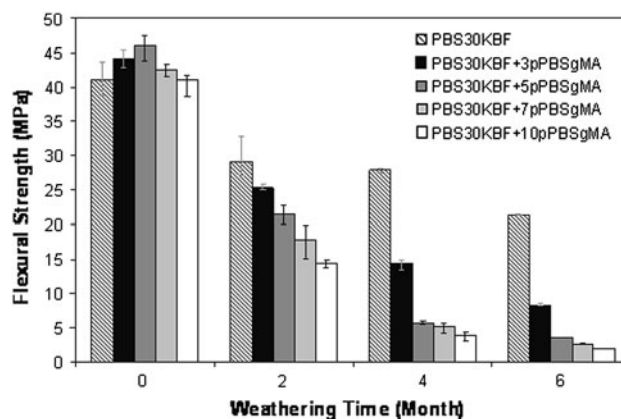

Fig. 3 Effect of natural weathering on the flexural strength of PBS30KBF composites with the addition of purified compatibilisers

Fig. 2 Effect of natural weathering on the flexural moduli of PBS and PBS/KBF composites with different fibre loadings
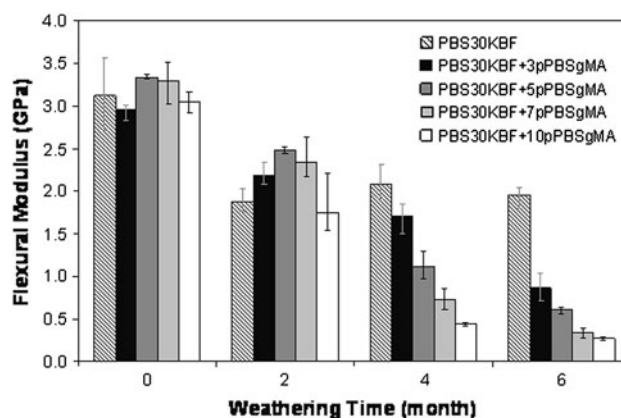

Fig. 4 Effect of natural weathering on the flexural modulus of PBS30KBF composites with the addition of purified PBSgMA

This can be associated with the presence of chemical groups in the compatibiliser that are more susceptible to undergo oxidation during exposure to natural weathering. Thus, the higher the concentration of MA in the compatibilisers, the composite degradation can be expected to be more severe. From Fig. 4 the tremendous decline in flexural modulus with increasing MA concentration in the compatibiliser at 4 and 6 months of exposure is probably due to extensive photo-degradation, chemical degradation and deterioration of fibre-matrix interfacial adhesion [14]. This degradation was also facilitated by the presence of moisture where the sorption and desorption cycle of water molecules during weathering led to the formation of voids, especially at fibre-matrix interface [19]. According to Muasher and Sain [1], photo-degradation that takes place during natural weathering will result in degradation of fibre components such as cellulose, hemicelluloses, lignin and extractives thus result in inferior composite properties. The deterioration of the composite structure is also accelerated by the cyclic expansion and contraction of the specimens resulting from fluctuating climatic conditions [17]. The presence of surface voids on the weathered surface will be shown later by SEM examination.

Colour Change

Effect of Natural Weathering on Colour Change

Table 3 shows the colour changes of PBS/KBF composites. Generally, the total colour change (ΔE_{ab}) of the weathered specimens increased with exposure time. This result is expected because the longer the exposure time, the more severe the surface degradation resulting from solar radiation [5]. As can be seen in Table 3, the neat PBS experienced the least colour change upon natural weathering,

with only about 2.8, 3.2 and 4.3 magnitude changes for 2, 4 and 6 months exposure periods, respectively. The neat PBS only experienced a slight colour change due to its original white colour, which makes it less susceptible to fading upon exposure to natural weathering. The ΔE_{ab} of the PBS/KBF composites increased with increasing fibre loading (Table 3). The increases are likely related to the shift of the lightness L of the unweathered composites to a darker magnitude with an increase in KBF loading. The increases in the darkness of unweathered specimens with increasing fibre loading confirms that the ΔE_{ab} of the composites are dominated by changes in the original specimen lightness and that the trend of ΔL seems to follow that of ΔE_{ab}.

The colour change of the composites is expected to be dominated by photo-degradation of the incorporated fibre constituents, namely cellulose, hemicellulose, lignin and extractives. The final colour of the composites is mainly influenced by the colour of the KBF because the original PBS colour is less faded upon natural weathering. According to Muasher and Sain [1], lignin will break down to water soluble products during natural weathering, eventually leading to the formation of chromophoric functional groups such as carboxylic acids, quinones and hydroperoxy radicals, thus causing discoloration in ligno-cellulosic material, mainly yellowing. As shown in Table 3, the yellowness (Δb) of the PBS/KBF specimens decreased at 4 and 6 months of exposure, indicating that the yellowing of the composites only occurred during the early stage of exposure. At 4 and 6 months of exposure the specimens are expected to undergo severe discoloration due to photo-bleaching of the chromophoric groups, usually resulting in the reduction of paraquinone to hydroquinone groups [1].

In contrast, the addition of pPBSgMA reduced the total colour changes of the composites to about 17.7–27.0% and

Table 3 Colour change for PBS, uncompatibilised composites (10–40 wt% KBF loading) and pPBSgMA compatibilised PBS30KBF

Specimen	Unweathered			ΔE_{ab}			ΔL			Δa			Δb		
				Weathering time (month)			Weathering time (month)			Weathering time (month)			Weathering time (month)		
	L	a	b	2	4	6	2	4	6	2	4	6	2	4	6
PBS	70.25	−1.45	3.47	2.80	3.22	4.30	1.95	2.59	3.87	−0.41	−0.39	−0.35	1.97	1.87	1.86
PBS10KBF	36.12	1.84	7.30	4.24	9.91	11.46	4.17	9.87	11.39	−0.52	−0.38	−0.56	0.55	−0.84	−1.12
PBS20KBF	32.50	2.09	6.76	8.40	14.83	16.94	8.35	14.76	16.87	−0.76	−1.15	−1.21	0.49	−0.93	−1.01
PBS30KBF	29.16	1.96	6.21	13.90	20.49	24.38	13.88	20.44	24.32	−0.67	−0.91	−1.47	0.30	−0.99	−0.91
PBS40KBF	28.38	1.82	5.69	16.12	21.90	26.48	16.09	21.84	26.44	−0.93	−1.21	−1.16	0.26	−1.10	−0.97
PBS30KBF(3p)	30.48	1.72	6.20	11.44	16.40	24.65	11.43	16.34	24.49	−0.48	−0.66	−1.39	0.10	−1.24	−2.36
PBS30KBF(5p)	29.85	1.76	6.26	11.16	15.68	23.22	11.15	15.60	23.05	−0.48	−0.81	−1.53	0.13	−1.43	−2.31
PBS30KBF(7p)	31.08	1.95	6.29	10.68	12.80	22.20	10.67	12.63	22.02	−0.47	−0.94	−1.66	0.20	−1.88	−2.25
PBS30KBF(10p)	31.09	1.98	6.29	10.14	12.83	22.50	10.13	12.61	22.34	−0.48	−1.06	−1.69	0.17	−2.16	−2.14

20.0–37.5% for the 2 and 4 months of exposure, respectively. This result indicates that the addition of the compatibilisers increased the colour stability of the composites. Perhaps the reaction between the OH groups of the fibre and the compatibiliser reduced the amount of free OH groups in the composites, which are known to be susceptible to photo-oxidation during natural weathering. However, after 6 months of exposure, the ΔE_{ab} of the uncompatibilised and compatibilised composites increased but the difference in ΔE_{ab} among the composites became smaller. This result indicates that all the composites have an approximately similar final colour because they were severely faded to a chalky white colour after exposure to natural weathering for a period of 6 months.

FTIR Spectroscopy Analysis

Figure 5 shows FTIR spectra of unweathered and weathered neat PBS. The latter shows increasing peaks at bands of 1,709, 952 and 914 cm^{-1} corresponding to formation of carbonyl and vinyl groups upon exposure to natural weathering. The peak at 1,709 cm^{-1} belonging to carbonyl species (carboxylic acid) seems to slightly increase with increasing weathering time. The increase of the 1,709 cm^{-1} peak with weathering time probably related to an increase in carbonyl products due to the formation of carboxylic, aldehyde and ketone species [13, 22]. Peaks corresponding to vinyl group observed at 952 and 914 cm^{-1} seem to increase with weathering time due to scission of the PBS main chains. As reported by Zou et al. [20] the exposure of polymer (i.e. HDPE) to UV light during weathering will result in carbonyl degradation via
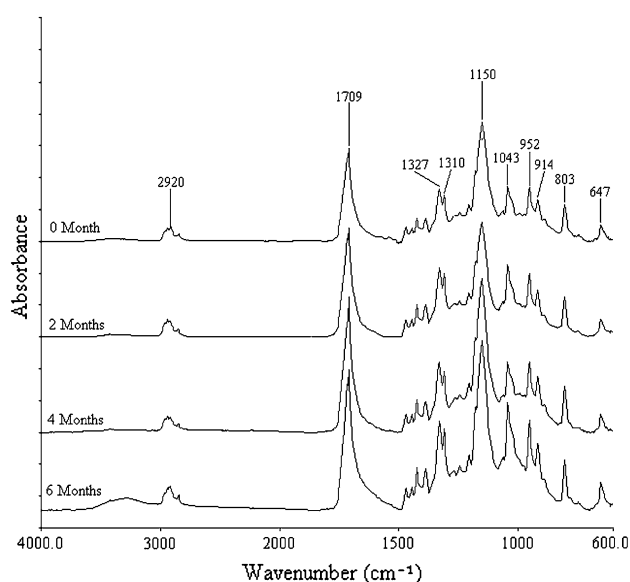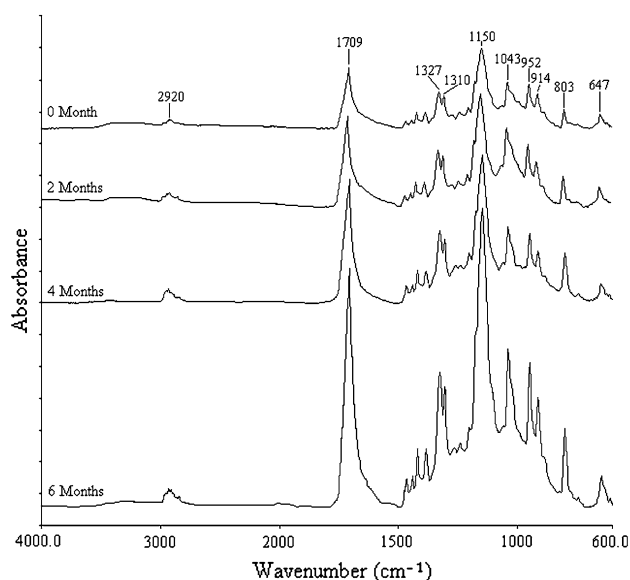
Fig. 6 FTIR spectra of PBS30KBF composites at various exposure times

Norrish type II which could be indicated by increasing in vinyl group concentration. As seen in Fig. 5 a weak shoulder appeared in the range of 3,200–3,600 cm^{-1} in the spectrum of 6 months weathered PBS. This probably due to presence of hydroxyl groups from the generation of hydroperoxide and hydroxyl species [18].

Figures 6 and 7 show FTIR spectra of unweathered and weathered uncompatibilised and compatibilised composites, respectively. Generally, the intensities of peaks corresponding to hydroxyl (3,200–3,600 cm^{-1}), carbonyl (1,709 cm^{-1}) and vinyl (914 and 952 cm^{-1}) species for the

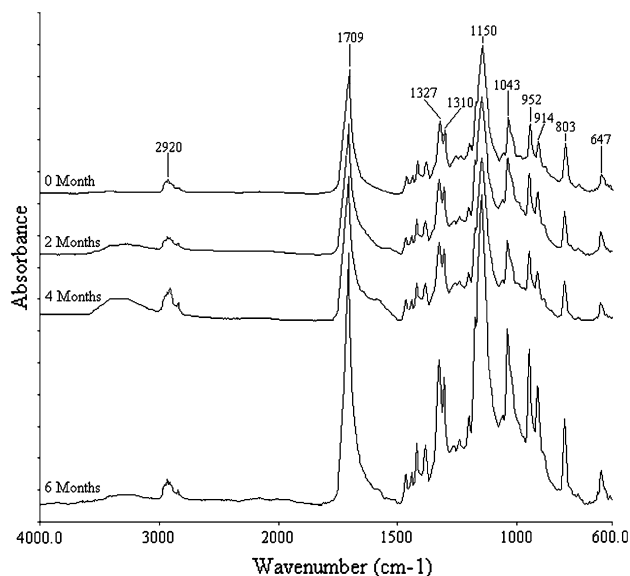Fig. 5 FTIR spectra of neat PBS at various exposure times

Fig. 7 FTIR spectra of PBS30KBF composites compatibilised with 5pPBSgMA at various exposure times

Table 4 Hydroxyl, carbonyl and vinyl indexes of PBS and PBS/KBF composites for various exposure times

Indexes	Hydroxyl index (HI)				Carbonyl index (CI)				Vinyl index (VI)			
Weathering time (months)	0	2	4	6	0	2	4	6	0	2	4	6
PBS	0.2	0.2	0.3	0.8	5.8	7.5	8.4	7.4	2.7	3.2	3.6	3.7
PBS30KBF	0.2	0.6	1.0	0.9	5.9	8.3	10.8	12.7	3.6	4.6	4.7	5.9
PBS30KBF + 5pPBSgMA	0.3	0.7	2.1	1.0	9.2	10.0	11.3	14.4	4.0	5.1	6.7	6.8

weathered uncompatibilised and compatibilised composites were higher than those of the unweathered composites. These peaks are very well defined and their intensities increased with increasing weathering time. The increases of the carbonyl peaks intensity could be associated with the presence of oxidation products such as a mixture of carboxylic acid and ketone species [23].

As shown in Figs. 6 and 7 the weathered uncompatibilised and compatibilised composites show increasing of peak intensities at 914 and 952 cm^{-1} band which correspond to vinyl groups, respectively. According to Mendes et al. [22], the occurrence of terminal vinyl groups was ascribed to the chain scission reaction of the polymer chains. However, the degradation of PBS/KBF composites may not have been directly influenced by the chain scission of the PBS main chains, but it could also be due to the degradation of the KBF constituents. Stark et al. [13] also found that the formation of vinyl group upon weathering is

a result of carbonyl degradation due to polymer chain scission in both matrix and natural fibre. Normally, the formation of vinyl group is a little bit delay in the early stage of natural weathering followed by steep increase as weathering time increase due to degradation polymer matrix via the Norrish type II mechanism [13]. As reported by Tidjani et al. [23], vinyl groups ($CH_2=CH-$) may also appear in the unsaturated region between 800 and 1,000 cm^{-1}; they could appear at 909 cm^{-1} along with trans-vinylene ($-CH=CH-$) at 965 cm^{-1} and vinylidene ($CH_2=C<$) at 988 cm^{-1}.

As shown in Figs. 6 and 7, exposure of the uncompatibilised and compatibilised composites to natural weathering led to the appearance of a new weak shoulder peak in the range of 3,200 to 3,600 cm^{-1} as early as 2 months of exposure. Previously, Li et al. [21] in PP/nano CaCO$_3$ system also reported the appearance of a new shoulder peak at 3,400 cm^{-1} after the composites were exposed to
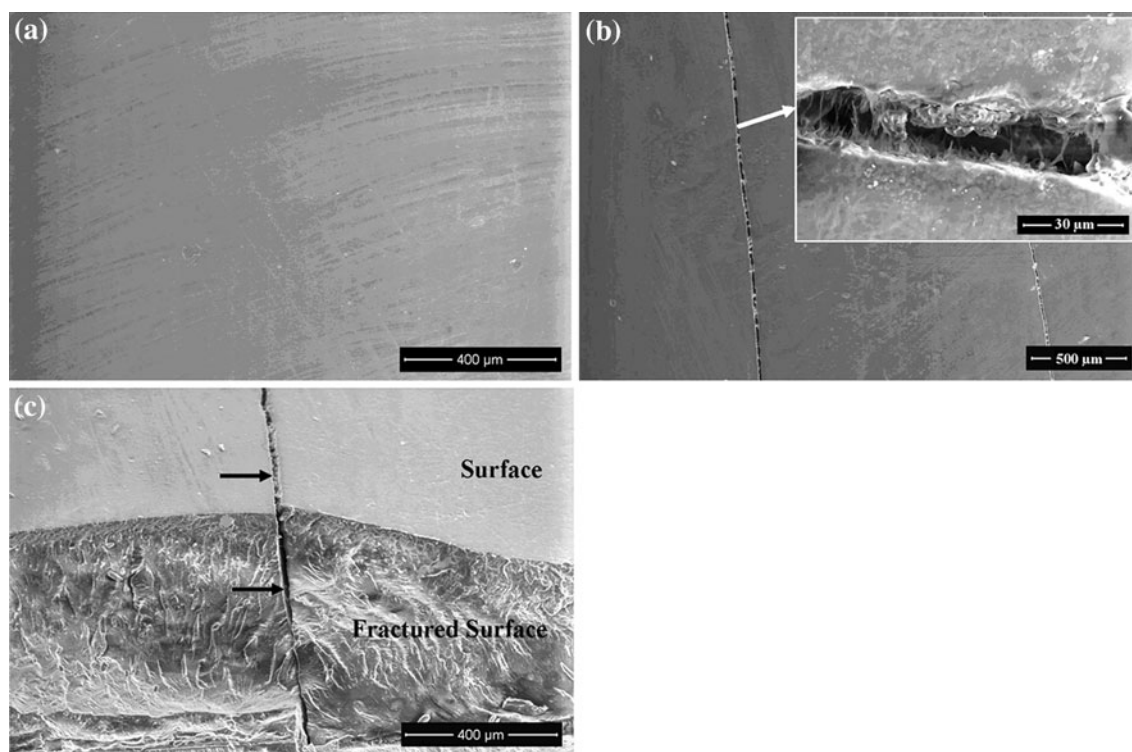

Fig. 8 SEM micrograph of **a** unweathered neat PBS (200× magnification) and 6 months weathered neat PBS, **b** surface (100× and inset: 3000× magnification) and **c** side view (200× magnification)

UV aging due to the generation of hydroperoxide and hydroxyl species. However, Stark and Matuana [24] in the weathering study of HDPE/wood flour composites reported the appearance of a broad shoulder peak at 3,200–3,400 cm^{-1} represent –OH stretching of lignocellulosic fibres that exposed on the weathered surface. In the case of compatibilised composites, the shoulder peak that appeared within the hydroxyl region (3,200–3,600 cm^{-1}) increased until achieve optimum increment at 4 months of weathering before decrease at 6 months of weathering. The reduction of the shoulder intensity was probably due to degradation of lignocelluloses constituent mainly polysaccharides [25]. Besides the reduction of the shoulder intensity could also be related to the loss of fibre on the weathered surface either blown away by wind or wash away by rain during the weathering. This observation also in agreement with that reported by Williams et al. [3] where the loss of surface particles were also observed on weathered wood.

As shown in Table 4, the compatibilised composites have the highest increment in hydroxyl, carbonyl and vinyl indexes for all weathering times followed by uncompatibilised composites and neat PBS. Generally, this indicates both of the composites experienced severe degradation during the 6 months of natural weathering compared to neat PBS. From Table 4 it can be seen that the carbonyl index (CI) of the neat PBS only increased at 2 and 4 months of exposure before decreased at 6 months of exposure. The decrease in the CI value at the prolonged exposure was associated with the formation of vinyl group. According to Stark et al. [13] the formation of vinyl group upon weathering is resulted by the carbonyl degradation consequences to polymer chain scission in both matrix and natural fibre. These results were also in line with the vinyl index of the neat PBS where the values steeply increased with the weathering time. As seen in Table 4 both CI and VI values for uncompatibilised and compatibilised composites increased with weathering time. These results indicate that the degradation of the composites became severe at prolonged weathering time. This probably due to the presence of KBF in the composites which is known could undergo severe degradation upon natural weathering. According to Stark and Matuana [13] the incorporation of natural fibre in polymer composite will increase the amount of oxygen including carbonyl functionality thus makes the composites more susceptible to undergo degradation. The degradation of the natural fibre was also accelerated by the presence of moisture [6] and the cyclic expansion and contraction of the specimens resulting from fluctuating climatic conditions [17]. In the case of composites with maleated compatibilisers, the addition of the compatibiliser is believed could decrease the durability of the composites against weathering exposure. According to Abu-Sharkh

and Hamid [14], the poor durability of compatibilised composites against natural weathering is due to the presence of chemical groups in the compatibiliser that are more susceptible to undergo oxidation.

It also can be seen that the hydroxyl index (HI) of PBS tremendously increased at 6 months of weathering. This probably due to the presence of hydroxyl groups from the generation of hydroperoxide and hydroxyl species after exposed to a prolonged weathering time [21]. The increases of HI for uncompatibilised and compatibilised composites observed at 2 and 4 months of weathering probably associated with the exposure of the KBF as a result of surface cracking. However the decreases of HI for uncompatibilised and compatibilised composites at 6 months of exposure probably due to degradation of natural fibre component mainly polysaccharides [25] and loss of fibre on the specimen surface either blown away by wind or wash away by rain after being exposed to a long period of weathering.

Surface Observation

Figure 8a shows SEM micrograph of the unweathered neat PBS surface. Cosmetic defects, i.e., scratch marks were
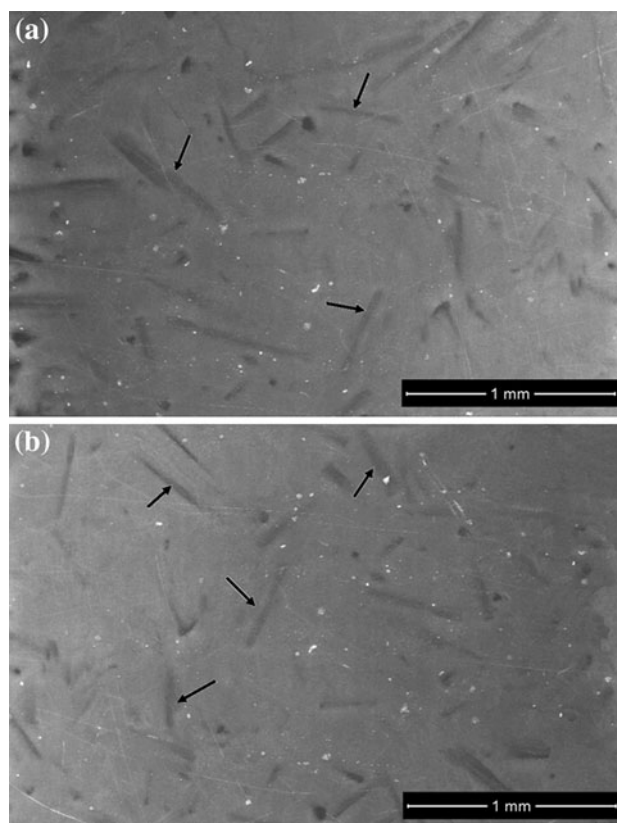

Fig. 9 SEM micrograph of the surfaces of unweathered **a** PBS30KBF and **b** PBS30KBF compatibilised with 5pPBSgMA composites at 50× magnification

revealed on the specimen surface due to an uneven mould surface and dirty mould covers. However, these defects should not affect the mechanical properties of the specimens. Figure 8b and c show that the neat PBS surfaces seem to be severely deteriorated after exposure to 6 months of natural weathering, with some large cracks (as marked by arrows) appearing on the weathered surface. Crack formation probably occurred due to thermal contraction and material loss during natural weathering. As shown by the inset of Fig. 8b and the fractured surface view of Fig. 8c, surface cracks were propagating deeply into the inner part of the specimen. Leong et al. [26] also observed the existence of deep cracks in weathered PP specimens after exposure to 6 months of natural weathering.

Figure 9a and b show the surface appearance of unweathered and weathered PBS30KBF composites. The embedded KBF appears as dark lines in the SEM micrographs and the fibres are in a random orientation distribution. The appearance of tiny white deposits (as marked with arrows) on the surface probably represents impurities (i.e., woody debris and dust) that either come from the surrounding material or are carried along by the KBF. Figure 10a and b show micrographs of the surface of the 6 months weathered PBS30KBF composite. The surface looks rougher as compared to unweathered composites. The weathered surfaces seem to be severely deteriorated, with microcracks covering the entire composite surface. Some white deposits (as marked with arrows) were also noted on the weathered surface. The white deposits are believed to originate from the degraded surface substance or from the low molecular weight polymer products of photo-oxidation [6, 14]. A closer examination of the weathered surface (Fig. 10b) revealed that the surface cracks exposed the embedded fibres to the specimen surface. Perhaps the surface cracks were initiated by swelling of the embedded fibres. The fibre swelling that occurred at extends of natural weathering due to absorption of moisture from environment [19]. The hygroscopic nature of the KBF and deterioration of fibre structure at extend of weathering increased the moisture absorption and thus facilitate the formation of severe cracks of the composites. In addition, the reduction of matrix phase ductility as a result of photo-oxidation and the cyclic effect of expansion and contraction of the specimens during natural weathering are also expected to accelerate the deterioration of the composite properties [17, 22].

Figure 10c and d show SEM micrographs of the surfaces of PBS30KBF composite compatibilised with 5pPBSgMA after 6 months exposure to natural weathering. As seen in Fig. 10c, many micro-cracks and tiny holes are present on the weathered surface. The severe surface erosion seems to indicate that the presence of PBSgMA compatibiliser failed to improve the durability of PBS30KBF composites under
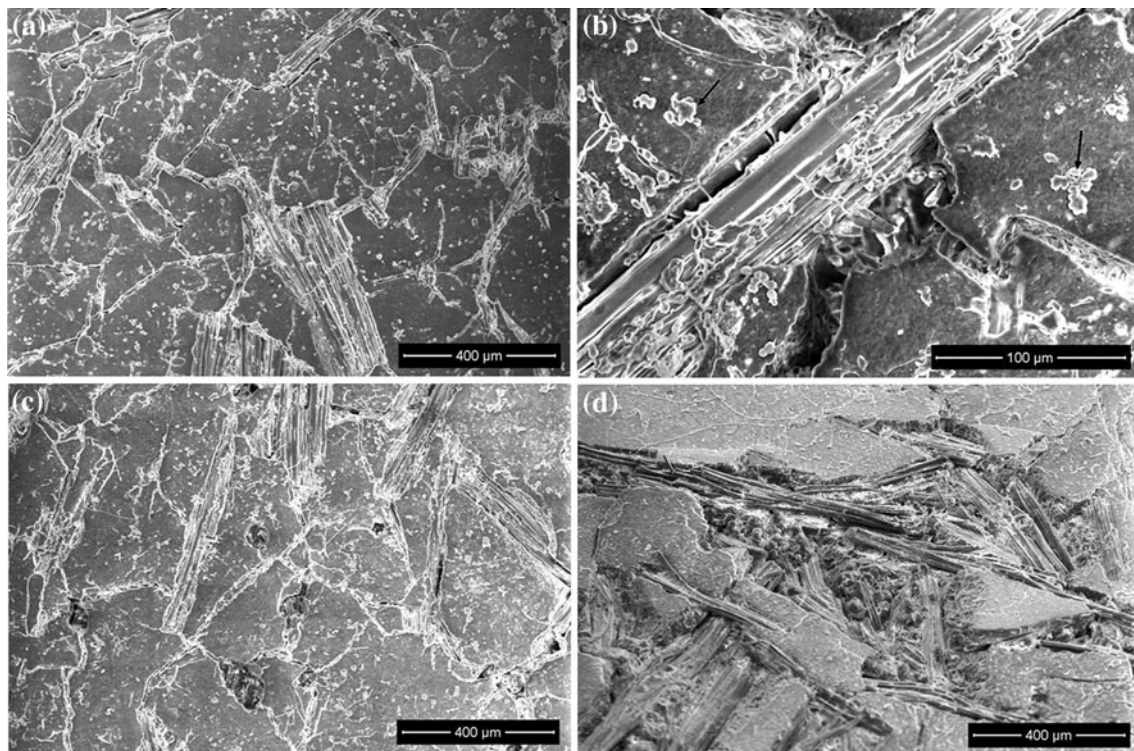

Fig. 10 SEM micrograph of 6 months weathered PBS30KBF composite surface at **a** 200× and **b** 1000× magnification and PBS30KBF composite compatibilised with 5pPBSgMA at **c** 200× and **d** 200× (side view) magnification

natural weathering. According to Abu-Sharkh and Hamid [14], the addition of maleated compatibiliser reduces the resistance of composite against natural weathering because the compatibiliser contains chemical groups that are more susceptible to oxidation than the polymer itself. The presence of tiny holes on the weathered surface probably result from the loss of degraded surface substances such as the detachment of low molecular weight polymer matrix and degraded natural fibre [1, 5]. The number of surface cracks for the compatibilised composite was also higher than that of composite without compatibiliser.

Conclusions

This study investigated the effect of KBF loading and maleated PBS compatibiliser addition on the natural weathering properties of PBS/KBF composites. Exposure of the composites to natural weathering reduced the flexural properties of the composites. The flexural properties of the composites decreased with an increase in the KBF loading due to the poor resistance of the fibre to natural weathering and the greater presence of composite imperfections. The addition of maleated PBS compatibiliser seems to reduce the retention of composite flexural properties upon natural weathering, and the drop in flexural strength became worse with an increase of the MA concentration in the compatibiliser. This effect of compatibiliser was attributed to the number of chemical groups that could undergo oxidation during natural weathering. Examination of the colour change confirmed the degradation of the composite, and the SEM examination revealed the deterioration of the composite structure after exposure to natural weathering for a period of 6 months.

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