Effect of Maleated Compatibiliser (PBS-g-MA) Addition on the Flexural Properties and Water Absorption of Poly(butylene succinate)/Kenaf Bast Fibre Composites
(Kesan Penambahan 'Maleated Compatibilizer' (PBSgMA) ke Atas Sifat Fleksur dan Penyerapan Air Komposit Poli(butilena suksinat)/Gentian Kulit Kenaf)

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ABSTRACT

Poly(butylene succinate) (PBS) composites with 30 wt.% loading of kenaf bast fibre (KBF) were compatibilised with 5 wt.% maleated PBS (PBS-g-MA). The maleic anhydride (MA) concentration in the compatibiliser was either 3, 5, 7 or 10 phr. In general, the compatibilised composites showed better flexural properties than the un-compatibilised composite. The highest increment in the flexural strength and modulus of 12.7 and 8.9%, respectively, were obtained with the addition of PBS-g-MA with MA concentration of 5 phr. Compatibilised and un-compatibilised PBS/KBF composites were immersed in distilled water for 90 days. The absorption of water by all the composites was observed to follow Fick's law. The equilibrium moisture content, M_m, of the composites with PBS-g-MA at 3, 5 and 7 phr of MA concentrations was lower than that of the un-compatibilised composite due to improved fiber-matrix interfacial adhesion and reduction of voids content. Both un-compatibilised and compatibilised composites showed dimensional instability after the water absorption. This was probably due to the degradation of the fibre-matrix interfacial adhesion and fibre integrity. The flexural properties of these composites decreased after the water absorption. After re-drying only some of the flexural properties were recovered from plasticizing effect of water.

Keyword: Composites; dimensional stability; interfacial adhesion; mechanical properties; water absorption

ABSTRAK

Komposit poli(butilena suksinat) (PBS) dengan pembebanan 30% berat gentian kulit kenaf telah ditambah dengan 5% berat 'maleated PBS' (PBSgMA). Kepekatan maleik anhidrida (MA) dalam penserasi yang digunakan ialah 3, 5, 7 atau 10 phr. Secara umumnya, komposit yang ditambah dengan penserasi menunjukkan sifat fleksur yang lebih baik berbanding komposit tanpa penserasi. Peningkatan kekuatan dan modulus fleksural yang tertinggi iaitu sebanyak 12.7 dan 8.9% telah diperoleh oleh komposit dengan penambahan PBSgMA dengan kepekatan MA 5 phr. Komposit PBS/KBF dengan dan tanpa penserasi telah direndam dalam air suling untuk tempoh 90 hari. Penyerapan air oleh semua komposit adalah mengikut Hukum Fick. Kandungan lembapan pada keseimbangan, M_m bagi komposit dengan penambahan PBSgMA pada kepekatan MA 3, 5 dan 7 phr adalah lebih rendah berbanding komposit tanpa penserasi kerana kesan penambahbaikan pelekatan antara muka gentian-matriks dan pengurangan kandungan lompang-lompang dalam komposit. Kedua-dua komposit tanpa dan dengan penserasi menunjukkan ketidakstabilan dimensi selepas penyerapan air berlaku. Ini adalah kerana degredasi pelekatan berlaku antara muka gentian-matriks dan integriti gentian. Sifat fleksural komposit-komposit itu juga menurun selepas penyerapan air. Selepas proses pengeringan sampel, hanya sebahagian sifat fleksural diperoleh semula.

Kata kunci: Kestabilan dimensi; komposit; pelekatan antara muka; penyerapan air; sifat mekanik

INTRODUCTION

Recently, the development of biodegradable polymers for fulfilling new ecological requirements and overcoming the environmental problem caused by the disposal of plastic materials are being explored. The use of these biodegradable polymers for substituting traditional non-biodegradable polymers is restricted due to their relatively high cost. This reason makes the incorporation of natural fibre appears to be an ideal solution for reducing the cost of end products yet promising environmental friendliness. In this study, poly(butylene succinate) PBS a semi-crystalline biodegradable aliphatic thermoplastic polyester, which is produced via the polycondensation reaction of 1,4-butanediol and succinic acid was used as the matrix. PBS was proven to undergo degradation in compost, moist soil, fresh water with activated sludge and seawater (Fujimaki 1998). Studies on lignocellulosic fillers (i.e. olive and spruce husk flour and flax) filled PBS composites have been reported by several researchers (Baiardo et al. 2004; Kim et al. 2005). However, very few studies were reported on kenaf bast fibre (KBF) filled PBS composites. Malaysian government has identified kenaf as a potential crop to be commercially farmed. Due to its high fibre strength and modulus which are comparable with hemp, ramie and jute

fibres, KBF appears to be suitable for reinforcing polymer composites (Bismarck et al. 2005).

The incompatibility issue between the hydrophilic KBF and the hydrophobic thermoplastic matrix usually limits the composite performance (Kim et al. 2005). The adhesion between fibre and matrix can be improved by adding compatibilisers. For PBS composites, the addition of maleated PBS compatibiliser that was produced by grafting of MA onto PBS through melt grafting with the presence of peroxide based free radical initiator has been reported to improve the interfacial adhesion and filler distribution in polymer matrix (Kim et al. 2005; Mani & Bhattacharya 2001).

In order to ensure durability of natural fibre filled thermoplastic composites for outdoor applications, it is crucial to evaluate the water absorption behaviour of the composites (Najafi et al. 2007; Tajvidi et al. 2006). The incorporation of lignocellulosic fibres has been known to increase the moisture affinity of the composites resulting in undesirable effect to the mechanical properties and dimensional stability. The deterioration effect of water on the properties of lignocellulosic fiber-polymer composites depends on the duration of the exposure. In the present study, compatibilised PBD/KBF composites were immersed in water for 90 days. The effect of water absorption on the flexural properties and dimensional stability of the composites were determined. Water absorption characteristics of the composites were also reported.

MATERIALS AND METHODS

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

Reactive mixing of maleated compatibiliser was carried out by using a Brabender internal compounder with co-rotating double winged rotors at 140°C with 50 rpm rotor speed for a total period of 5 min. PBS, DCP and MA were pre-mixed thoroughly before feed into the compounding chamber. Four formulations of

compatibiliser were introduced as listed in Table 1. The reactively mixed compatibilisers were purified by refluxing in chloroform for 1 h. Then the reflux solution was poured into cold methanol and filtered. The precipitated polymer was then washed with fresh methanol to remove residual of unreacted MA and DCP. Finally, the polymer was dried in an oven at 80°C for 24 h. Prior to use, the compatibiliser was kept in desiccators. The grafting degree of the purified compatibilisers was determined by titration of acid groups derived from the anhydride functional groups as suggested by Zhu et al. (2006); the results are presented in Table 1.

The control composite was compounded according to the formulation, 30 and 70 wt.% KBF and PBS while the compatibilised composites were compounded according to formulation 30, 65 and 5 wt.% of KBF, PBS and PBS-g-MA by using a Brabender internal mixer with co-rotating double winged rotors. Temperature of the compounding chamber was set at 130°C. Generally, PBS and the compatibiliser were physically pre-mixed before loading into the chamber. Then the weighted fibre was added gradually into the chamber under low rotor speed (10 rpm). Once all the fibres were fed in, the compounding process was continued at 50 rpm rotor speed for 5 min before being discharged. The composite compounds were compression moulded at 130ºC into specimens with a dimension of 120 × 12 × 3 mm^3 using a compression moulding machine (model Kao Tieh Gotech). The moulding cycle involved 5 min of pre-heating without pressure, 3 min of compression under 150 kg/cm^3 of pressure and 5 min of cooling under the same pressure. The moulded specimens were kept in desiccators prior to test.

Flexural tests were performed on the dry, wet and redried (drying treatment at 70ºC for 24 h) specimens at the end of 90 days water immersion to verify the retention and recovery of the composites. Flexural test in three-points bending mode were performed using a universal testing machine (model Instron 3366) with a load cell of 10 kN according to ASTM D 790-86. The test was carried out in accordance with ASTM D 790-86 at span length of 50 mm and cross-head speed of 5 mm/min. The data were presented in averaged values of 5 measurements.

The water absorption study was carried out by direct immersing of PBS and PBS/KBF composites in distilled water at room temperature for a period of 90 days according to ASTM D570. Prior to immersion, the specimens were dried in an oven at 80°C to a constant weight. The weights of

TABLE 1. Formulation and grafting degree for maleated compatibilisers

PBS-g-MA	Formulation (phr)			Grafting degree (%)
	PBS	MA	DCP	
3PBS-g-MA	100	3	1	0.91 ± 0.03
5PBS-g-MA	100	5	1	1.07 ± 0.02
7PBS-g-MA	100	7	1	2.14 ± 0.04
10PBS-g-MA	100	10	1	2.32 ± 0.05

the specimens were measured at regular intervals and the water absorption at t time (M_t) was calculated by:

$$M_t(\%) = \frac{W_2 - W_1}{W_1} \times 100, \qquad (1)$$

where, W_1 and W_2 are the weight of the specimen before and after immersion, respectively. The water absorption characteristics were expressed by two parameters, the diffusion coefficient, D, and the equilibrium water content, M_m. The percentage of equilibrium water content, M_m, was determined once the specimen achieves a saturation point. From the experimental curve of the water content at t, time, M_t versus the square root of the immersion time, $t^{1/2}$, the diffusion coefficient, D, can be calculated from the initial portion of the curve using the following:

$$D = \frac{\pi h^2 \left(M_2 - M_1\right)^2}{16 M_m^2 \left(t_2^{1/2} - t_1^{1/2}\right)^2}, \qquad (2)$$

where M_1, and M_2 are the water contents at times t_1 and t_2, respectively. M_m is the maximum water content or equilibrium water content and h is the thickness of the specimen.

The dimensional stability of the specimen upon water immersion was determined by measuring the thickness swelling. The thickness swelling was calculated by:

$$\text{Thickness swelling } (\%) = \frac{t_w - t_d}{t_d} \times 100, \qquad (3)$$

where t_d and t_w are the specimen thickness before and after immersion. The thickness swelling was measured by vernier caliper to the accuracy of 0.01 mm and the value was presented as averaged values of 3 specimens.

Morphological studies of water immersed specimens' surfaces and flexural fracture surfaces were carried out on low vacuum mode scanning electron microscope (model FEI Quanta 200). The specimens were used as prepared.

RESULTS AND DISCUSSION

FLEXURAL PROPERTIES

Figure 1 shows the effect of compatibiliser on the flexural properties of PBS/KBF composites with fibre loading of 30 wt.%. In general, the compatibilised composites have higher flexural strength than the un-compatibilised composite (control) due to improvement of the fiber-matrix interfacial adhesion. According to Tserki et al. (2006), the formation of cohesive fiber-matrix interfacial adhesion is attributed to the ability of the MA to react with the hydroxyls group of the lignocelluloses and good compatibility of the grafted copolymer chains with the main polymeric phase. It is interesting to note that the compatibilised composites achieved optimum flexural strength with increment of about 12.7% when the compatibiliser had a 5 phr concentration of MA.

An increase in the MA concentration of the compatibiliser also resulted in moderate increment in the flexural modulus before attain the maximum increase of 8.9% at an addition of compatibiliser with 5 phr concentration of MA (5PBS-g-MA). Further increase in the MA concentration i.e. 7 and 10 phr, resulted in the slight decrease of flexural modulus. The decrement might be due
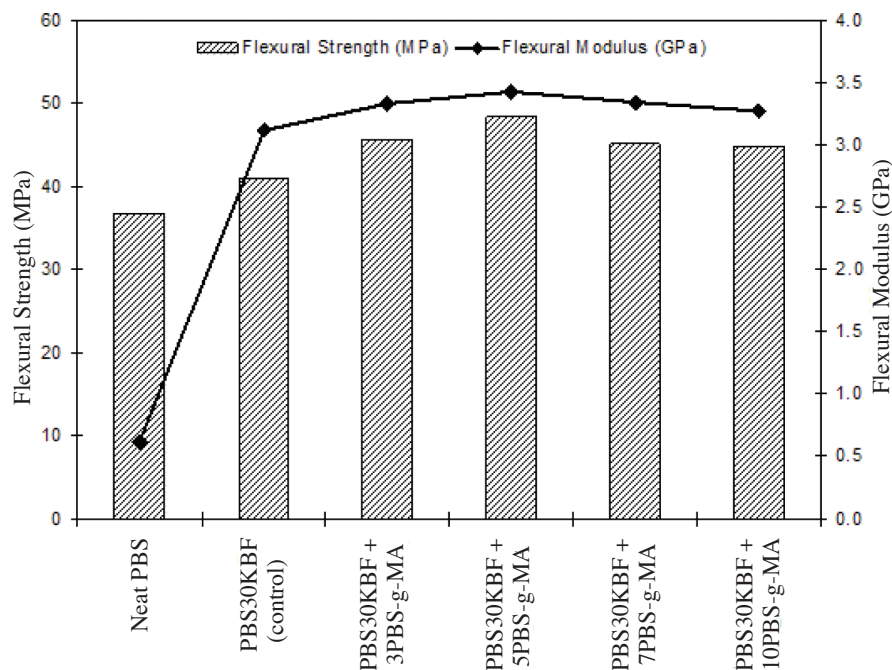

FIGURE 1. Effect of PBS-g-MA addition on the flexural strength and modulus of the PBS30KBF composites

to the deterioration of compatibiliser intrinsic properties i.e. strength and modulus as a result of severe chain scission during the grafting process in the presence of high concentration of MA. From the flexural properties, it is confirmed that the 5PBS-g-MA is the best compatibiliser for the PBS/KBF composite system. According to Mani and Bhattacharya (2001), the ideal compatibiliser must have optimal degree of grafting with minimal polymer chain degradation and significant enhancements in the fiber-matrix interfacial adhesion.

Figure 2 shows the water absorption of un-compatibilised and compatibilised composites after 90 days of water immersion. Rapid water absorption was observed for both un-compatibilised and compatibilised composites during the early stage of immersion. After which, the water absorption of the composites seems to increase gradually with time until it achieves saturation. This trend shows that the kinetics of water absorption of the composites follows to Fick's diffusion behaviour. The diffusion coefficient, D of the samples was calculated from the initial portion of the curve using (2). The neat PBS has a very low D value compared with un-compatibilised and compatibilised composites due to the hydrophobic nature of the polymer (Table 2). On the contrary, the compatibilised composites have slightly higher D values in comparison with the un-compatibilised composite and the values seem to increase with increasing concentration of MA in the compatibilisers. Since the D values were measured during the initial stage of immersion, the results may reflect the permeability of the matrix layer to water molecules. The increase of D values were probably related

TABLE 2. Diffusion coefficient of neat PBS and PBS30KBF composites

Specimen	Diffusion Coefficient, D ($\times 10^{-11}$ m^2/s)
PBS	0.19
PBS30KBF (control)	2.37
PBS30KBF + 3PBS-g-MA	3.18
PBS30KBF + 5PBS-g-MA	3.43
PBS30KBF + 7PBS-g-MA	3.67
PBS30KBF + 10PBS-g-MA	3.24

to the presence of more hydrophilic sites in the matrix phase as 5 wt.% fraction of the PBS matrix was substituted by the compatibiliser. It is known that the MA group has 3 oxygen sites which could possibly form hydrogen bond with water molecules during immersion.

The compatibilised composites with MA concentrations of 3, 5 and 7 phr have lower equilibrium water content values in comparison with the un-compatibilised composite (Figure 2). It is believed that the addition of purified compatibilisers into the composites improved the fibre-matrix interfacial adhesion and reduced the void content leading to a decrease in the absorption of water by the composites. According to Mat Taib et al. (2006) the decrease in equilibrium water content of a composite with the addition of maleated compatibiliser may be attributed to the restriction of free movement water molecules within the composite structure due to cohesive fibre-matrix adhesion, fewer free hydroxyl group of fibre left because
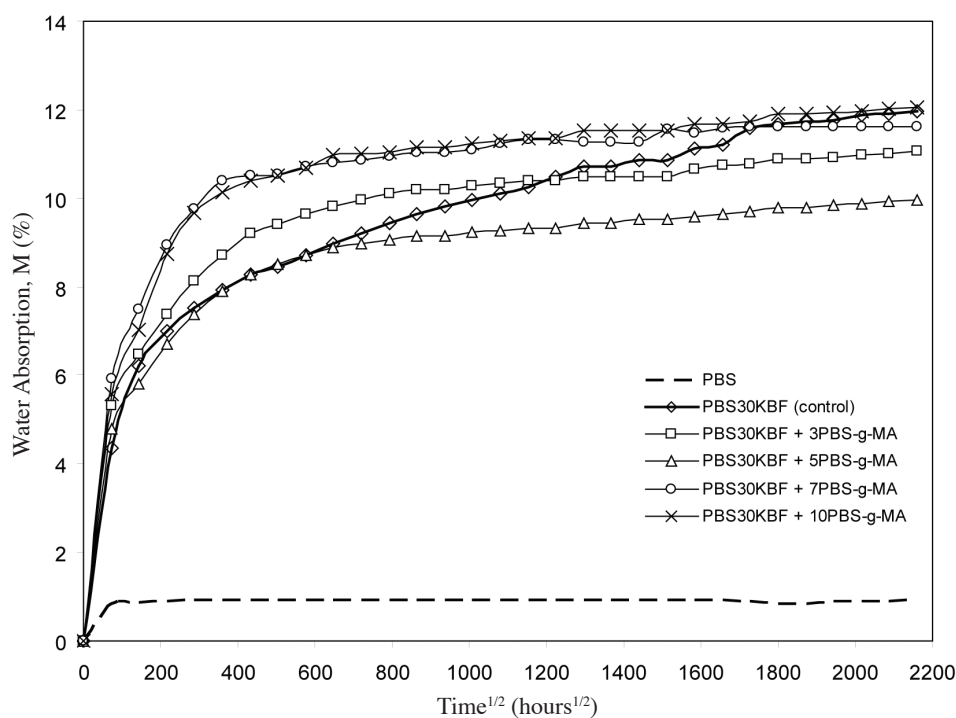

FIGURE 2. Effect of compatibilisers on the water absorption of PBS30KBF composites during 90 days of immersion

most of them covalently bonded to the functional groups of MA and introduction of compatibiliser resulted in better coating of the fibres with polymer matrix thus protect the hydroxyl groups of the fibre to come in contact and form hydrogen bond with water molecules. The findings of this work are in agreement with the findings of other works such as Najafi et al. (2007) and Tserki et al. (2006).

The dimensional stability of PBS and compatibilised PBS30KBF composites upon 90 days water immersion is presented as thickness swelling in Figure 3. From this figure, the neat PBS does not show any appreciable increment in thickness swelling due to the hydrophobic characteristic of the polymer. On the contrary, all the un-compatibilised and compatibilised composites show increments in thickness swelling during the immersion due to the presence of 30 wt.% of hydrophilic KBF. In this case, all the composites were exposed to water exceeded the induction stage and this is the reason why all the composites have experienced significant changes in thickness swelling at the end of the exposure. This observation was in agreement with that reported by Chow et al. (2007) and the occurrence of dimension instability was due to the damage of the fiber-matrix interface and fibre integrity.

The thickness swelling of the composites increased with the incorporation of 5wt.% maleated PBS (Figure 3). In comparison between un-compatibilised and compatibilised composites, only composites with addition of 3PBS-g-MA and 5PBS-g-MA compatibilisers have comparable thickness swelling while composites with compatibilisers of 7PBS-g-MA and 10PBS-g-MA have slight higher thickness swelling by 3.1 – 4.1%. This result indicated that incorporation of compatibilisers with high concentration of MA i.e. 7 and 10 phr resulted in significant dimensional instability of the composites. Perhaps the presence of higher concentration of MA increased the number of carbonyl group thus resulted in greater water affinity. In this condition, deteriorating effect of water on the composite structure becomes aggravated. This observation also in agreement with that report by Mat Taib et al. (2006).

Table 3 presents the effect of 90 days water immersion and drying treatment on the flexural properties of un-compatibilised and compatibilised composites. In general, both composites experienced tremendous drop in flexural properties after water absorption for a period of 90 days. It can be seen for the compatibilised composites that the percentage drop in strength and modulus increased between
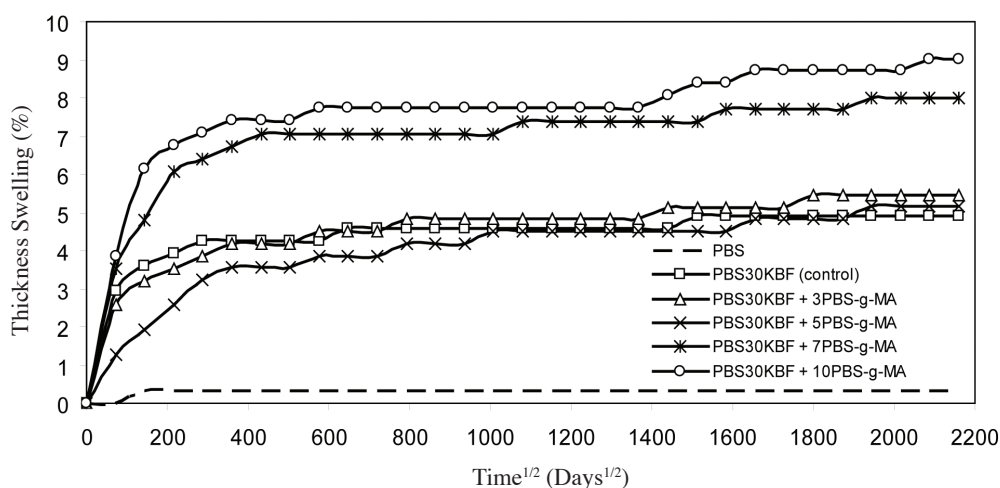

FIGURE 3. Effect of compatibilisers addition on the thickness swelling of
PBS30KBF composites during 90 days of immersion

TABLE 3. Flexural properties of PBS and PBS30KBF composites after 90 days water
immersion (wet) and drying treatment (redried)

Material	Flexural strength (MPa)			Flexural modulus (GPa)		
	Dry (Control)	Wet[a]	Redried[b]	Dry (Control)	Wet[a]	Redried[b]
Neat PBS	36.8	37.1 (-0.8)	37.6 [102.1]	0.62	0.74 (-18.82)	0.79 [127.42]
PBS30KBF(control)	42.9	18.5 (56.9)	28.3 [66.0]	3.15	2.04 (35.32)	2.19 [69.37]
PBS30KBF+3PBS-g-MA	45.8	13.6 (70.4)	19.9 [43.4]	3.00	1.77 (40.92)	1.84 [61.44]
PBS30KBF+5PBS-g-MA	48.4	14.8 (69.4)	22.3 [46.1]	3.43	1.75 (48.88)	1.79 [52.19]
PBS30KBF+7PBS-g-MA	45.3	10.3 (77.2)	13.8 [30.5]	3.35	1.75 (47.76)	1.82 [54.43]
PBS30KBF+10PBS-g-MA	44.8	9.9 (77.7)	11.3 [25.1]	3.28	1.79 (45.43)	1.81 [55.18]

[a]The values in parentheses ( ) are the percentage drop of flexural properties after immersion
[b]The values in brackets [ ] are the percentage recovery of flexural properties after immersion

69 and 78% and 41 and 45%, respectively, with increasing MA concentration. Due to the hydrophobic nature, the neat PBS did not show any appreciable changes in flexural properties as it was not deteriorated by the water. According to Mat Taib et al. (2006) the drop in composites properties with and without compatibiliser upon water immersion therefore could probably be due to the deteriorating impact of the interactions between water molecules and the lignocellulosic fiber and/or the interface region. In this case, the addition of 5 wt.% compatibiliser appeared to be unable to prevent deterioration of the composite strength and modulus against the long period of water immersion i.e. 90 days.

The effect of redrying on the 90 days water immersed specimens was conducted to determine the residual of flexural properties after drying treatment at 70ºC for 24 h. The redried composites have higher flexural strength in comparison with wet composites (Table 3). These results indicated that the composites properties were partially restored after being exposed to drying treatment. The recovery of the composite properties upon exposed to drying treatment normally contributed by restoration of plasticizing effect of water molecules (Espert et al. 2004). However, the recovery of properties is rather minimal due to the deterioration of both the fibre-matrix interface and the fibre integrity (Chow et al. 2007).

From Figure 4(a) and 4(b), it can be seen that some random distributed dark stripes appeared on both surfaces of un-compatibilised and 5PBS-g-MA compatibilised composites indicated that no fibres exposed on the un-immersed composite surfaces. On the contrary, severe micro-cracks clearly appeared on both surfaces of un-compatibilised and compatibilised composites after being exposed to 90 days of water immersion (Figure 5(a) and 5(b)). The cracks seem to propagate throughout the entire composite surface. These SEM micrographs show the evidence for poor dimensional stability and mechanical properties of the composites upon the 90 days water immersion. Furthermore, the deterioration of wet 5PBS-g-MA compatibilised composite surface was more severe than that of wet un-compatibilised composite, where the formation of larger cracks, holes and exposed fibres could be noticed on the surface. This qualitative information reflects the poor dimensional stability and flexural properties of compatibilised composites in comparison with the un-compatibilised composite after being exposed to the water immersion.

CONCLUSION

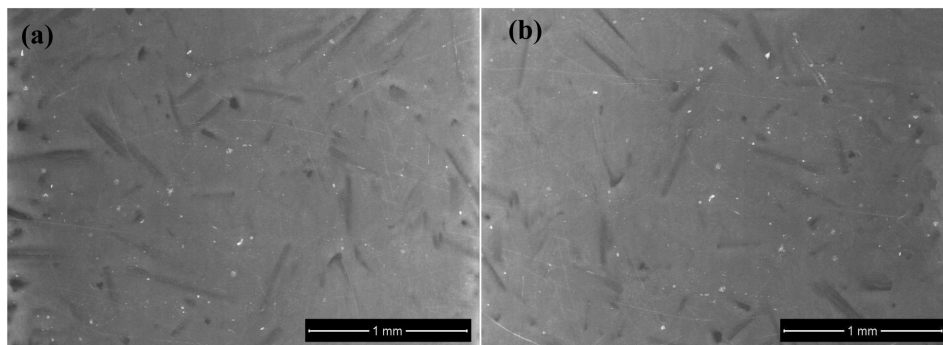The ideal compatibiliser for PBS30KBF composite was 5PBS-g-MA and the compatibilised composite with 5 wt.%

FIGURE 4. SEM micrographs of PBS30KBF composites (a) without and (b) with 5PBS-g-MA compatibiliser before being exposed to 90 days of water immersion
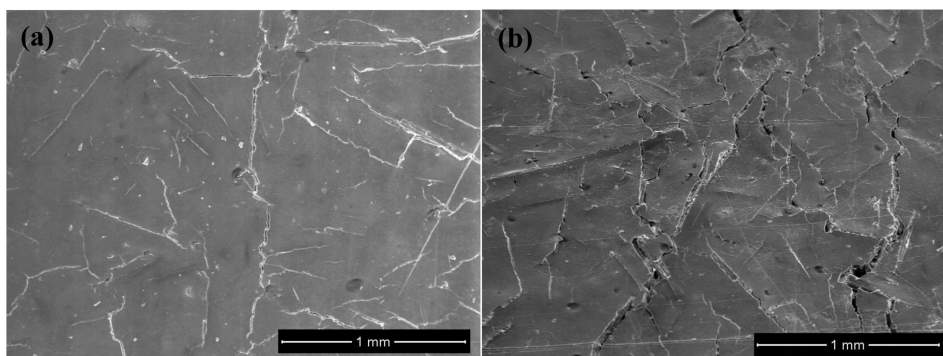

FIGURE 5. SEM micrographs of PBS30KBF composites (a) without and (b) with 5PBS-g-MA compatibiliser after being exposed to 90 days of water immersion

of the compatibiliser showed the highest increment in the flexural properties. The addition of the maleated PBS with low concentration of MA i.e. 3 & 5 phr resulted in lower equilibrium water content than the un-compatibilised composites but comparable in the thickness swelling. Prolong period of water absorption resulted in severe deterioration of the flexural properties of both un-compatibilised and compatibilised composites due to the degradation of composite constituent, matrix, fibre and interface between them. Some of the flexural properties were recovered after the drying treatment due to the recovery of plasticizing effect of the water molecules.

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