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Mechanical and Thermal Characterization of Polyester Composite Containing Treated Wood Flour from Palm Oil Biomass

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The effect of water and alkali treatment on the thermal decomposition of oil palm shell (OPS) together with the mechanical performance of polyester composites reinforced with treated OPS has been presented in this work. Treatment of OPS with cold/hot distilled water and cold alkali treatment were found to improve the tensile and flexural strength of the resulting composites although the highest mechanical performance was noted with the use of sonication in hot distilled water. On the other hand, hot alkali treatment was found to produce a composite mechanical performance similar to that of the hot distilled water treatment with sonication. FTIR tests indicated that adsorbed water molecules together with some parts of the hemicellulose and lignin were removed by the treatments. Thermogravimetric analysis and scanning electron microscopy of the treated OPS with hot alkali (1–9% concentration) showed that the mechanical performance reach a peak at 7% alkali concentration with a further increase in concentration resulting in a significant lignin mass loss and decrease in mass residue of the OPS. This trend was attributed to the higher alkali concentration removing hemicellulose as a binder for the cellulose and lignin which resulted in debonding between the filler and matrix components of the OPS and hence a deterioration in fiber structure and resulting poor composite mechanical performance. Therefore, it was concluded that the optimum concentration of alkali treatment required for maximum mechanical performance of natural filler reinforced polymer composites can be obtained simply from thermogravimetric analysis. POLYM. COMPOS., 00:000–000, 2016. © 2016 Society of Plastics Engineers

INTRODUCTION

Oil palm shell (OPS) is an agricultural solid waste produced from the palm oil industry in tropical regimes [1] with the significant amount of waste material produced by the oil palm industry having led to calls for an improvement in recycling. It is estimated that 6.89 million tons of OPS are produced annually as a byproduct of the oil palm industry with this number being expected to increase further [2]. While the majority of this byproduct is currently utilized as boiler fuel, other candidate applications include the use of OPS as a natural filler for the reinforcement of concrete and other composite materials [3]. The main advantages of utilizing OPS as a natural filler in polymer composite materials, in comparison to synthetic filler and fiber, are its low cost, low carbon dioxide emissions, reduced tool wear, low density, high-specific properties, noncorrosiveness, ease of separation, and reduced dermal and respiratory irritation [4].

In contrast to this, a main disadvantage of OPS as a natural filler within reinforced polymer composites is the low surface free energy of both the filler and polymer which tends to result in poor interfacial bonding between the filler and polymer matrix [5]. Physical and chemical treatment of the natural filler are common methods utilized to improve interfacial bonding between filler and matrix with physical treatment being known to alter the surface properties and structure of the filler without any change to chemical composition [6]. With regards to chemical treatment, water treatment of flax fibers has been noted to significantly increase interfacial shear strength with only a marginal decrease in tensile properties [7] whereas alkali treatment (also known as mercerization) is known to be an effective treatment for the removal of surface impurities together with the majority

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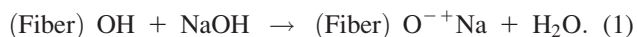
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TABLE 1. The physical properties of OPS [8, 9].

Properties	Specific gravity	Bulk density (kg/m ³)	Porosity %	Fineness modulus	Water absorption (24 h) (%)	Aggregate impact value (AIV) (%)	LA abrasion value (%)	Flakiness index (FI) (%)	Elongation index (EI) (%)
Value	1.14–1.62	590–740	28–37	6.41	24.3	2.11	5	41	59

of lignin, wax, and oils covering the reinforcement surface [10]. The increase in composite mechanical properties due to alkali treatment of the natural reinforcement has been attributed to better mechanical interlocking as a result of the increase of fiber surface roughness together with an increase in potential chemical reaction sites due to the increased amount of cellulose being exposed on the fiber surface [11]. It has been reported that the surface porosity and roughness of hydrophilic OPS particles could be enhanced by washing with methanol, which led to improved wettability by the hydrophobic polymer matrix [3]. The porosity and other physical properties of OPS are presented in Table 1.

It has also been reported that mercerization effects the degree of polymerization and cellulosic fibril due to removal of hemicellulose and lignin together with a reduction in amorphous hydroxyl groups according to the following reaction [7, 12]:



The thermal performance of natural fiber is a serious concern, especially in the case of the processing of natural fiber composites at elevated temperature, with this issue being attributed to the limited thermal stability of natural fibers [13]. Based on results previously obtained by the authors, chemical treatment had a significant effect on the thermal behavior of OPS. In addition to this, thermogravimetric analysis (TGA) in flowing oxygen revealed that the addition of OPS powder in isophthalic unsaturated polyester (UP) composites shifted the thermal degradation peak of the biocomposite to a higher temperature (from 370 to 418°C) [3].

In light of the above information, in the present work the authors have investigated the influence of chemical

treatment on the thermal behavior of OPS and the mechanical properties of unsaturated polyester composites reinforced with OPS filler.

EXPERIMENTAL PROCEDURE

Raw OPS material from Palm Oil biomass was utilized as the natural filler in this work with the OPS being first pulverized in a ball mill and then separated by mechanical sieving to produce OPS powder with a particle size in the range of 75–150 μm . Following this, the powdered OPS was chemically treated using distilled water and/or sodium hydroxide (NaOH) solution according to Table 2 and finally dried in an oven at 100°C for 2 h.

In the first stage of testing, the influence of different washing methods for OPS on the resulting composite properties was investigated by manufacturing isophthalic unsaturated polyester composites containing 5 wt% of OPS filler. The UP resin and OPS filler were gently mixed with 1.5 wt% of methyl ethyl ketone peroxide (MEKP) and then placed under vacuum to remove excess air bubbles. Following this, the mixture was poured into molds in order to produce five dumbbell and bar specimens according to ASTM D638 and ASTM D760 for tensile and flexural testing, respectively. The specimens were left to post cure at 80°C for 1 h prior to being removed from the molds. In the second stage of testing, the influence of alkali treatment on OPS filler was investigated by manufacturing UP composites containing 15 wt% of OPS powder treated with NaOH (1–9% concentration) at 90°C. In order to neutralize the aqueous system, all alkali treated samples were washed several times with distilled water until a pH of less than 8 had been achieved.

TABLE 2. Preparation conditions for the OPS powder specimens

Sample name	Step 1		Step 2	
	Solution	Conditions	Solution	Conditions
UT	–	Untreated	–	–
CDW	Distilled water	1 h at 25°C	–	–
HDW	Distilled water	1 h at 90°C	–	–
HDW-US	Distilled water	1 h at 90°C	Distilled water	High-frequency ultrasonic 30 min at 60°C then
CAT1	5% Sodium hydroxide	1 h at 25°C	Distilled water	Neutralize
CAT48	5% Sodium hydroxide	48 h at 25°C	Distilled water	Neutralize
HAT	5% Sodium hydroxide	1 h at 90°C	Distilled water	Neutralize

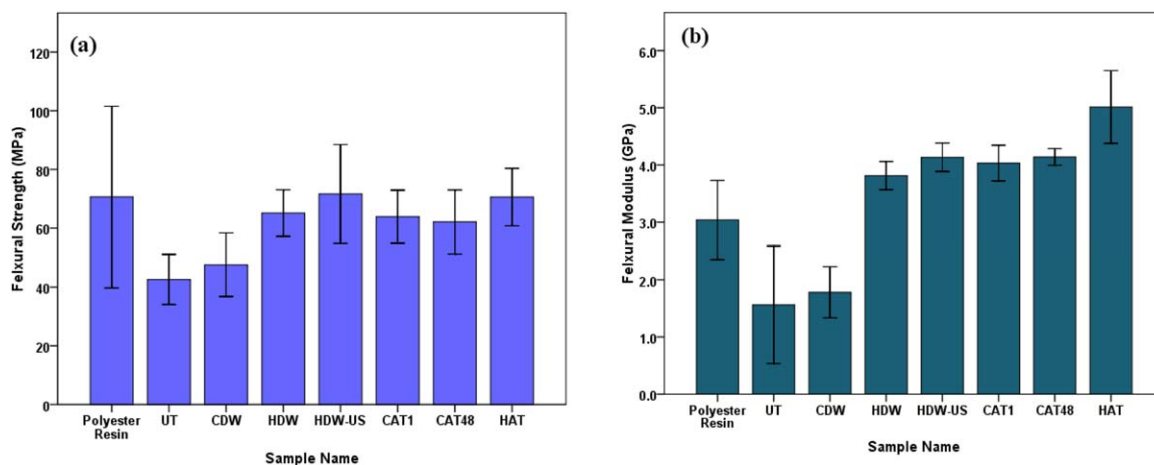


FIG. 1. Effect of OPS powder treatment on the flexural properties of isophthalic unsaturated polyester (UP) reinforced with 5 wt % of OPS: (a) strength and (b) modulus. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

The mechanical behavior of the composite specimens under tensile and flexural loading was investigated using a universal tensile testing machine (Lloyds instrument model LR10K Plus Digital Control Testing) at a cross-head rate of 2 mm min^{-1} . Tensile and flexural tests were carried using 10 kN and 500 N load cells, respectively, with the span to depth ratio for the three point bend flexural specimens being nominally 21.

Thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) analysis of OPS powder were used to measure the weight loss and thermal behavior of untreated and alkali treated OPS as a function of temperature. The analysis was conducted for a temperature range of $35\text{--}700^\circ\text{C}$ with a heating rate of $20^\circ\text{C min}^{-1}$ in an 80 mL min^{-1} flowing nitrogen atmosphere (Mettler Toledo TGA, Model; TGA/DSC1).

The FTIR spectra of OPS powder were obtained using an Agilent Cary 630 FTIR spectrometer. The FTIR tests were carried out between 650 and 4000 cm^{-1} with a resolution of 4 cm^{-1} .

Investigation of the OPS morphology and fracture surfaces of composite specimens was carried out using scanning electron microscopy (SEM; Hitachi S-3400N) with the surface roughness of the OPS and the quality of bonding between filler and matrix being determined.

RESULT AND DISCUSSION

Mechanical Properties

Effect of Different Treatment. In the present work, the influence of various washing treatments (as shown in Table 2) on the flexural strength and modulus of UP composites containing 5 wt % of OPS has been presented in Fig. 1. As shown in Fig. 1, the cold distilled water (CDW) washing method improved the flexural strength from 42.6 to 47.6 MPa (i.e., 11.7% increase) and flexural

modulus from 1.56 to 1.78 GPa (i.e., 14.1% increase) compared to the untreated (UT) case. This result is in good agreement with previous research [11] which indicated that water-soluble polysaccharides on the surface of hemp fiber could be effectively removed through the use of a cold water treatment. Figure 1 also indicates that the flexural strength could be further increased to 65.1 MPa using a hot distilled water (HDW) treatment—an improvement of 36.8% compared to the CDW case, while the flexural modulus exhibited an even greater increase of 114% compared to the CDW treatment. Based on Fig. 1 and results previously obtained by the authors [3] it can be concluded that HDW washing is more effective than methanol with the flexural strength and modulus being 8.00% (60.3–65.13 MPa) and 30.9% (2.91–3.81 GPa) higher, respectively, compared to methanol washed samples. Furthermore, sonication was noted to improve the flexural strength of the HDW-US composites by 10.0% (71.4 MPa) compared to the HDW case with a similar trend being observed for flexural modulus with an 8.4% increase to 4.13 GPa. These results were attributed to enhanced removal of surface impurities from the OPS powder through a combination of hot distilled water and sonication.

Figure 1 also illustrates the effect of time and temperature of alkali treatment of OPS powder on flexural properties of the resulting composites. For example, although the flexural strength and modulus following 1 h in 5% NaOH solution (CAT1) exhibited a slight improvement (1.9% for flexural strength and 5.2% for flexural modulus) compared to the HDW treated composite, the results were still lower than for the HDW-US case. Increasing the alkali treatment time to 48 h for the CAT48 composite decreased flexural strength by 2.72% (from 63.9 to 62.2 MPa) compared to the CAT1 composite although flexural modulus recorded a slight improvement to be comparable with the value of HDW-US case. In addition

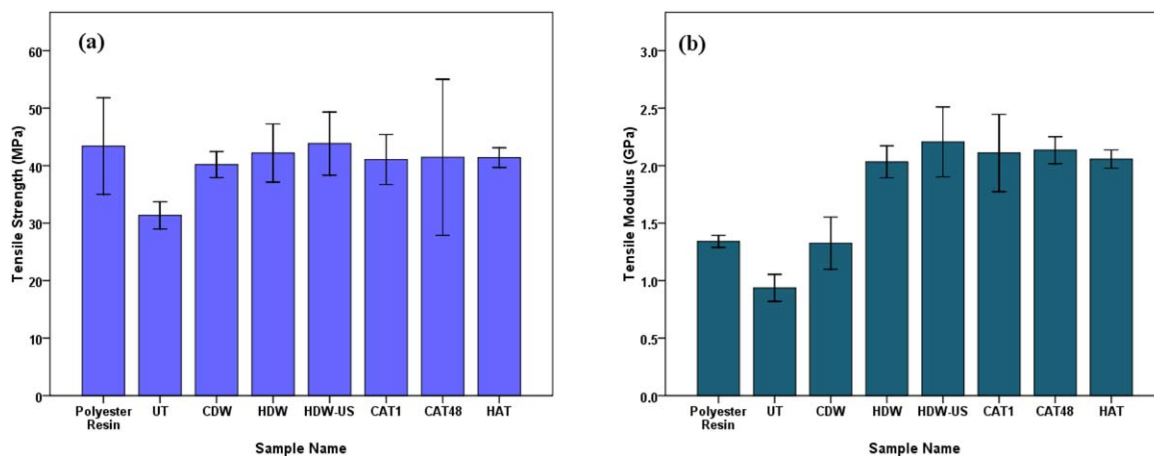


FIG. 2. Effect of OPS powder treatment on the tensile properties of isophthalic unsaturated polyester (UP) reinforced with 5 wt % of OPS: (a) tensile strength and (b) tensile modulus. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to this, flexural strength could be further increased to 70.6 MPa using a hot alkali treatment (HAT) with an improvement of 10.5% compared to the CAT1 case while the flexural modulus increased to 5.02 GPa (an improvement of 24.5% compared to the CAT1 treatment). In conclusion, the hot distilled water (HDW and HDW-US), cold alkali treatment (CAT1 and CAT48), and hot alkali treatment (HAT) all provided significant improvements in flexural properties compared to the cold distilled water treatment. It was also evident that effective washing by hot distilled water, which is promoted by sonication, provided flexural results similar or slightly higher than those obtained by alkali treatment (apart from the higher flexural modulus of the HAT composite).

The influence of OPS treatment on the tensile properties of resulting UP composites reinforced with 5 wt% of OPS has been presented in Fig. 2. However, compared to the flexural results, the variation in tensile strength for all OPS treatments was relatively minor (in comparison to the untreated case), although there is a suggestion that the alkali treatments were slightly less effective compared to the hot distilled water (with and without sonication) cases. This latter finding is in agreement with previous work on the tensile properties of wood plastic composites (WPC) [8] where the tensile strength and Young's modulus of the fibers deteriorated by alkali treatment due to a reduction in the degree of crystallinity and crystalline orientation.

Effect of Hot Alkali Concentration. The effect of hot alkali (NaOH) concentration (1–9%) on the tensile and flexural properties of isophthalic unsaturated polyester composites reinforced with 15 wt% of treated OPS powder has been presented in Fig. 3. It is clear from the results that the flexural strength (Fig. 3b) and modulus (Fig. 3d) reach their maximum values for the case of 7% NaOH concentration with the flexural strength increasing slightly from 66.1 MPa for the untreated (UT) composite to 76.7 MPa for

7% NaOH but then decreasing to 67.0 MPa for the 9% NaOH case. Flexural modulus exhibited a similar trend with a significant increase from 3.81 GPa for the untreated (UT) composite to 5.75 GPa for the 7% NaOH concentration composite and then followed by a decrease to 4.21 GPa for the 9% NaOH case. In contrast to this, the tensile strength (Fig. 3a) and modulus (Fig. 3c) did not appear to be improved by hot alkali treatment with an overall general decline in tensile strength and modulus with increasing hot NaOH concentration.

Morphological Study by SEM

Effect of Different Treatment. As mentioned earlier, it has been reported that the existence of surface impurities on OPS powder, as shown in Fig. 4, has a significant effect on reducing the mechanical properties of OPS-UP composites. It has been previously noted that the surface porosity and roughness of hydrophilic OPS particles could be enhanced by washing with methanol, which led to improved wettability by the hydrophobic polymer matrix [3].

Figure 5 illustrates the effect of different treatments on the surface morphology of OPS powder. From these micrographs, it appeared that hot distilled washing (Fig. 5a) increased the amount of solubility impurities, waxes, oils and water-soluble polysaccharides present on the surface of OPS powder compared to the cold distilled water OPS (Fig. 4). Figure 5b illustrates that sonication has a significant effect on the removal of the rest of the impurities and waxy materials from the surface of OPS in hot distilled water process, which increases the surface roughness as high as CAT1 (Fig. 5c). In addition, it is evident that the surface roughness in the HAT sample (Fig. 5d) is superior to that of the CAT1 treated powder (Fig. 5c) with this being attributed to increased removal of hemicellulose and lignin.

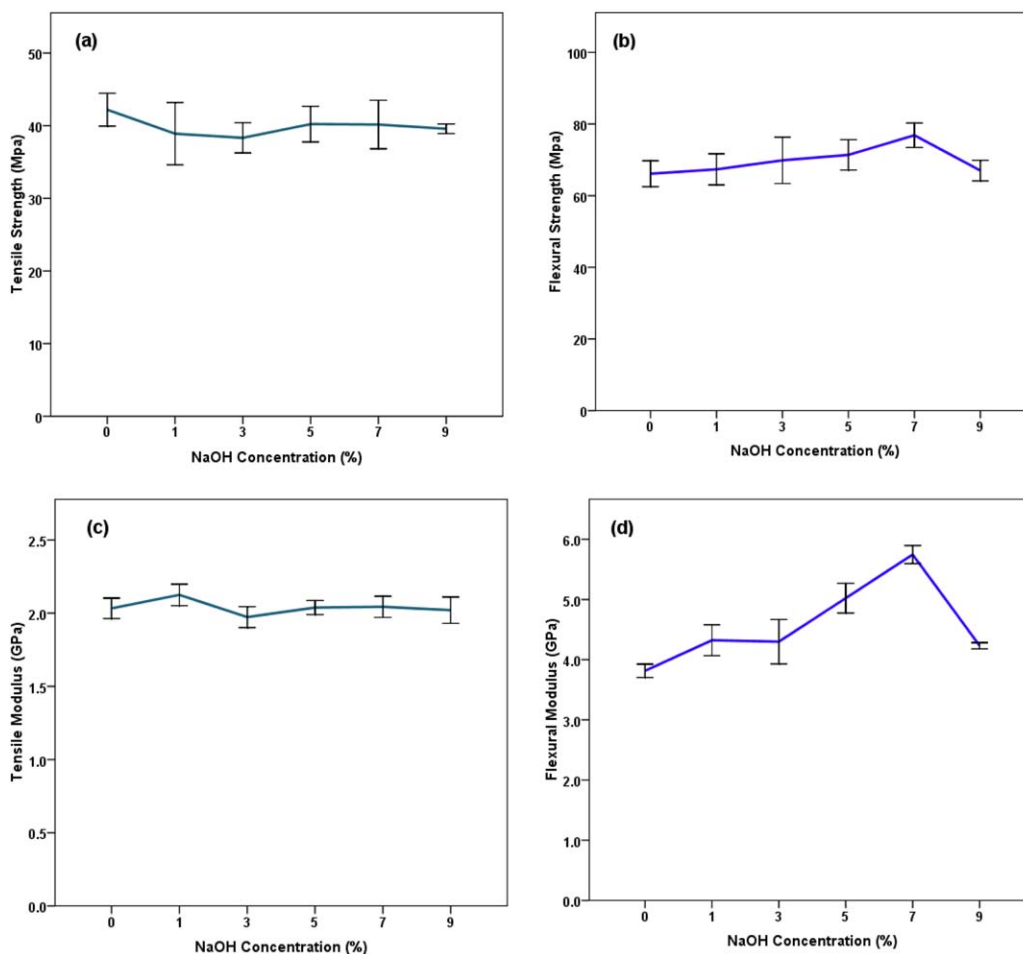


FIG. 3. Effect of sodium hydroxide (NaOH) concentration on the mechanical properties of an isophthalic unsaturated polyester (UP) composite reinforced with 15 wt % of hot alkali treated OPS powder: (a) tensile strength, (b) flexural strength, (c) tensile modulus, and (d) flexural modulus. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

It has previously been suggested that improved bonding between the OPS filler particles and UP matrix was due to effective polymer chain pinning [3]. Figure

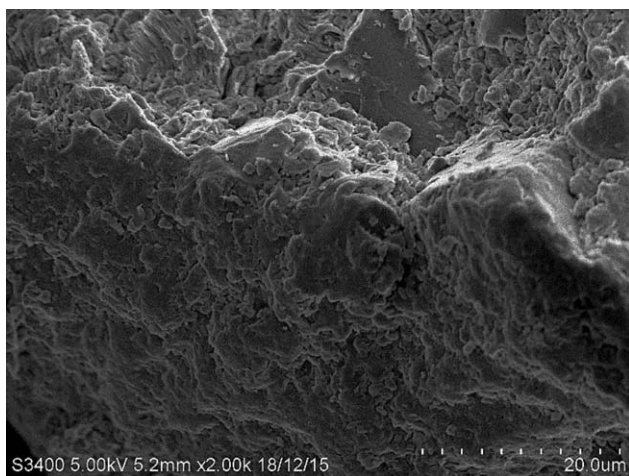


FIG. 4. Scanning electron micrograph of unwashed OPS powder.

6 illustrates fracture micrographs of UP composites reinforced with 5 wt% of washed OPS powder with obvious debonding between filler and matrix being noted in the cold distilled water composite (Fig. 6a) whereas interfacial bonding improved for the hot distilled water case (Fig. 6b) and it was superior for the hot distilled water with sonication (Fig. 6c). Thus, it is suggested that the mechanical performance of these composites can be improved due to better wettability between filler and matrix molecules as a result of eliminating impurities together with a portion of the hemicellulose and lignin.

While the surface roughness at the interface of filler and matrix was improved due to alkali treatment (Fig. 6d and e), it would appear that alkali treatment does not significantly improve interfacial bonding further than that already obtained using a hot distilled water treatment, especially for the case of the CAT1 treatment. Therefore, the mechanical properties of the composites were not improved significantly by alkali treatment when compared to hot distilled water treatment.

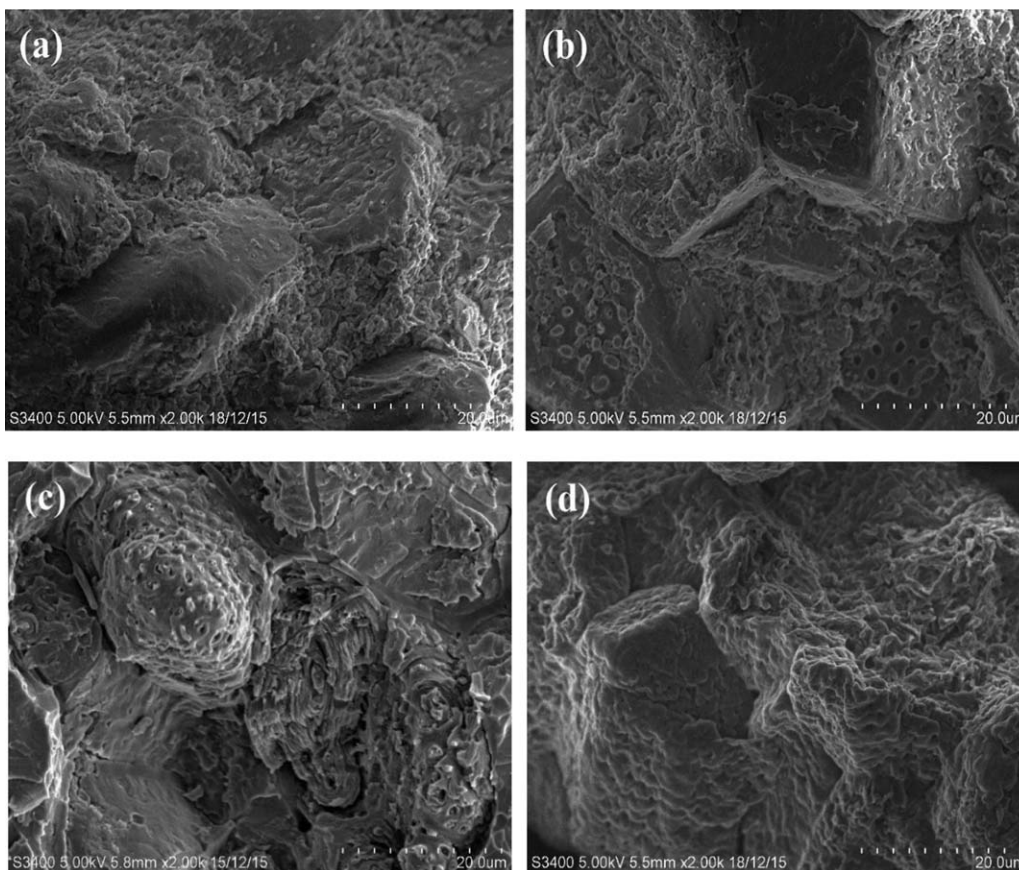


FIG. 5. Scanning electron micrographs showing the effect of washing treatment on the surface morphology of OPS powder: (a) hot distilled water (CDW), (b) hot distilled water with sonication (HDW-US), (c) cold alkali treated for 1 h (CAT1), and (d) hot alkali treated for 1 h (HAT).

Effect of Alkali Concentration. The influence of hot alkali treatment on the wettability of UP matrix by OPS powder has been presented in Fig. 7. It would appear that the quality of bonding between the powder and matrix was similar for the 1% hot NaOH treated composite (Fig. 7a) as for the hot distilled water treated composite (Fig. 6b). As expected from the mechanical property data (Fig. 3) the 7% hot NaOH composite (Fig. 7b) exhibited the best interfacial bonding behavior when compared to the 1% (Fig. 7a) and 9% (Fig. 7c) cases. These results are consistent with a previous study on the effect of alkali concentration on the mechanical properties of *Borassus* fruit fibers [14] which indicated that the maximum tensile properties of the fibers were attained with the maximum amount of α -cellulose, which itself was achieved for an optimum period of time (8 h) at 5% alkali treatment with the properties subsequently decreasing at more than the optimum time. This could also be attributed to the fact that the existence of surface impurities on the OPS powder, which has a significant effect on reducing the mechanical properties of OPS-UP composites, were removed by chemical treatment [3, 15]. The effect of chemical treatment on the removal of chemical molecules is investigated further in sections Fourier Transform Infra-

red Spectroscopy (FT-IR) and Thermal Behavior Study of OPS by Thermogravimetric Analysis.

Fourier Transform Infrared Spectroscopy

Lignocellulose materials are made of cellulose, hemicellulose, and lignin as the three main ingredients of natural fiber/filler from plant resources [16]. Cellulose with a general formula of $C_6H_{10}O_5$ is a linear and nonbranched macromolecule with 1–4-linked β -d-anhydroglucopyranose units which contains carbonyl, carboxyl and aldehyde groups [17–19]. In contrast to this, lignin consists of aromatic syringyl, guaiacyl, methoxyl, hydroxycinnamic, and methylene groups as highly branched aliphatic and phenolic structures. Hemicellulose contains different polysaccharides such as glucose, arabinose, xylenes, xylose, galactose, mannose, and ketone groups and is responsible for the generation of suitable linkages between cellulose and lignin by ether bonds of xylene molecule [19].

The functional groups of natural fiber can be identified by FTIR. The FTIR spectra of OPS before and after treatment are presented in Fig. 8. As shown in Fig. 8, some well-defined peaks show a slight difference after treatment in the fingerprint region between 1718 and

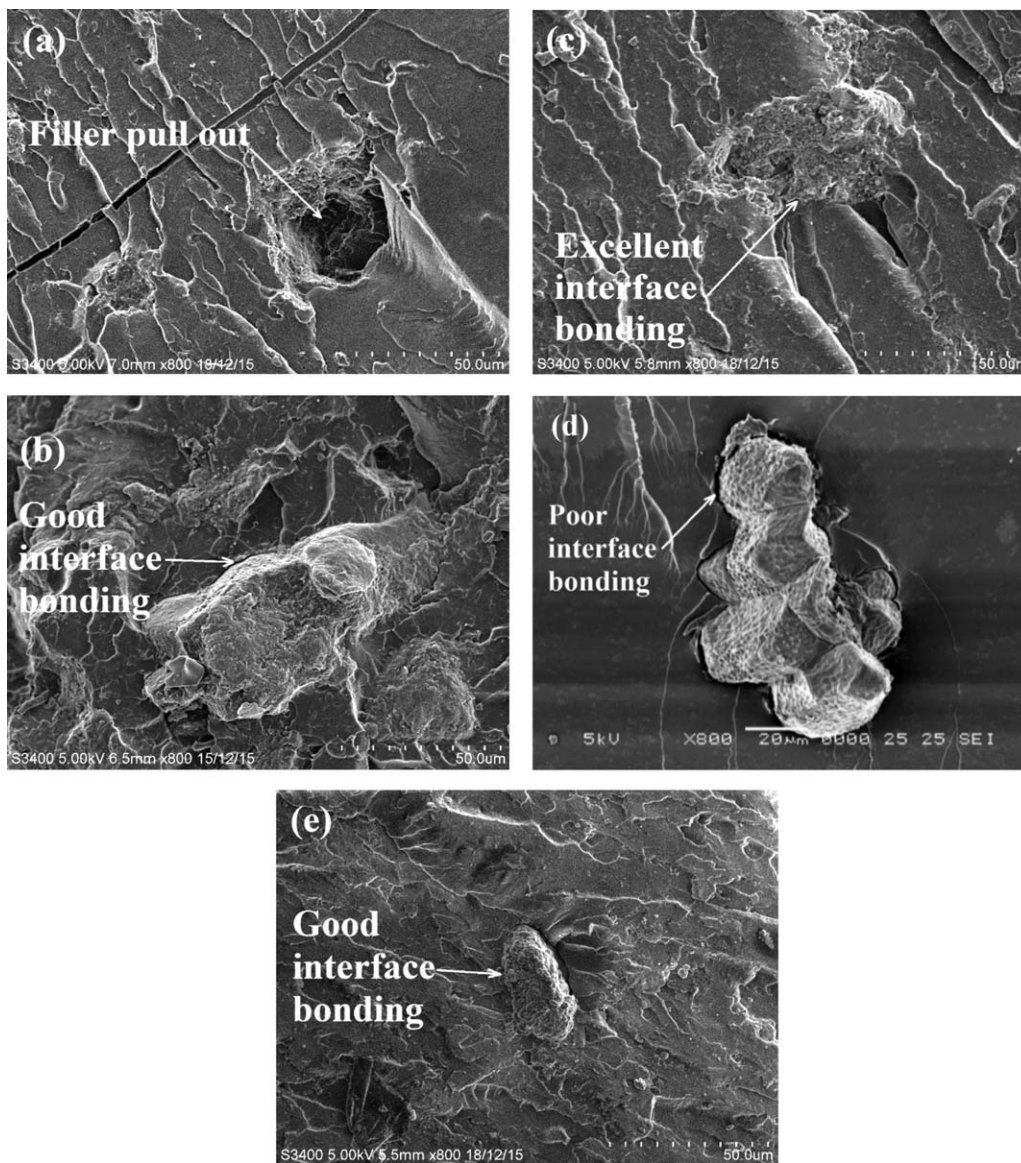


FIG. 6. Scanning electron micrographs showing the effect of washing treatment on the fracture morphology of isophthalic unsaturated polyester (UP) reinforced with 5 wt % of OPS powder: (c) cold distilled water (b) hot distilled water (HDW), (c) hot distilled water with sonication (HDW-US), (d) cold alkali treated for 1 h (CAT1), and (e) hot alkali treated for 1 h (HAT).

770 cm^{-1} . Based on Fig. 8, the peaks in the fingerprint region, which indicate related functional groups of OPS, are assigned in Table 3.

It has been shown that the characteristic peak at 1030 cm^{-1} was designated as the C—H in plane deformation of Guaiacyl in lignin and C—O stretch of primary alcohol and syringyl ring [20]. The intensity of the peak at 1030 cm^{-1} decreased by 17.3% (from 11.95 to 10.5) by hot water washing. This reduction was continued (by 26.7%) with sonication in hot water washed (HDW-US) OPS where the result was comparable with HAT treatment at the optimum concentration. This reduction indicates that sonication in hot distilled water was effective in removing Guaiacyl, Syringyl elements, and primary

alcohol molecules of lignin. Removal of Syringyl and Guaiacyl elements were confirmed by the reduction of peak intensities at 1239 and 1508 cm^{-1} , respectively. The removal of lignin parts were also observed by a 55.8% reduction in peak intensity at 1594 cm^{-1} which is attributed to C—C stretching of the aromatic rings of lignin. The carbonyl of aldehydes, ketones, and acetyl group in hydroxycinnamic acids associated with the alcoholic polysaccharides in lignin exhibit a peak at 1718 cm^{-1} [19, 21]. The intensity of this peak decreased by 21% in HDW-US and completely disappeared following hot alkali treatment. Consequently, it can be concluded that HDW and HAT are able to remove some chemical elements in lignin parts of OPS.

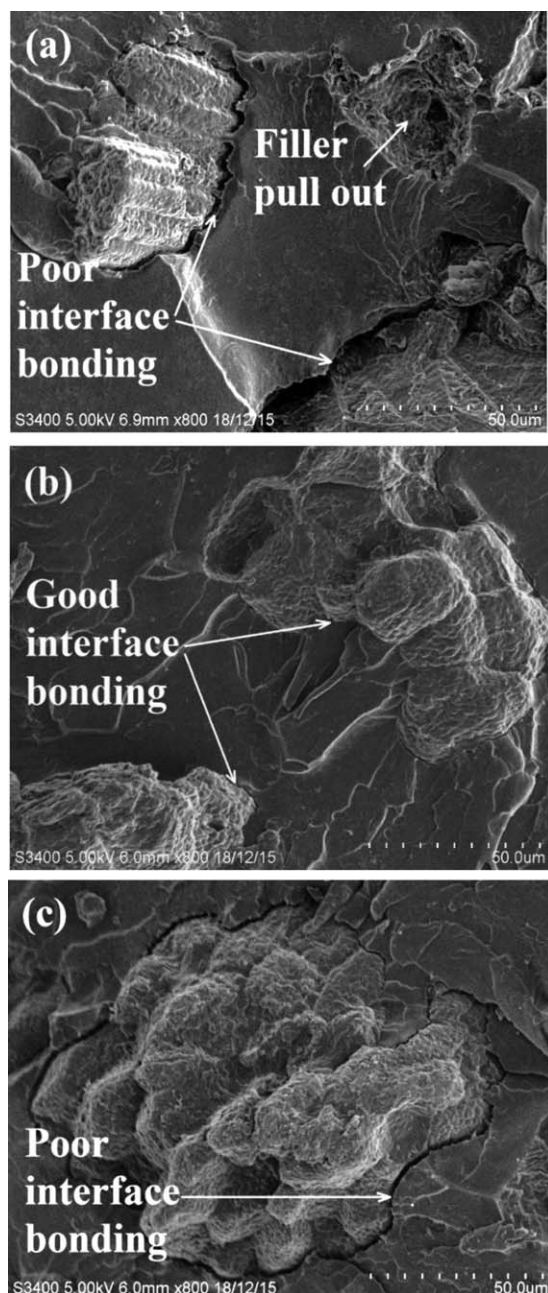


FIG. 7. Scanning electron micrographs illustrating the effect of sodium hydroxide (NaOH) concentration on the quality of interfacial bonding in an isophthalic unsaturated polyester (UP) composite reinforced with 15 wt % of hot alkali treated OPS powder: (a) 1%, (b) 7%, and (c) 9%.

Xylans are polysaccharides made from units of xylose and are a group of hemicelluloses [22]. Significant changes in FTIR spectra could be seen after treatment in the intensities of the unconjugated C=O (carbonyl) band in Xylan at 1239 and 1374 cm^{-1} [20, 23]. The intensities of the 1239 and 1374 cm^{-1} peaks decreased significantly with hot alkali treatment by 92.2 and 52.2%, respectively, with the peak positions shifting to 1244 and 1368 cm^{-1} . Furthermore, the intensity of the minor peak at 1654 cm^{-1} reduced significantly by hot alkali treatment, which is attributed to the C—H banding and C=O stretch-

ing frequency of Quinine, Quinine methides and adsorbed water in hemicellulose. The peak value at 1162 cm^{-1} is attributed to C—O—C symmetric stretching of hemicellulose and $\beta(1,4)$ -glycosic linkage for cellulose I and cellulose II [23]. The intensity of this peak was reduced at 7% HAT by 34%. Contrary to this, the relative intensities of the bands at 896 and 1420 cm^{-1} , which are refer to the C—H bending of amorphous and crystalline cellulose respectively [19], get stronger by hot alkali treatment. This indicates that hot alkali treatment did not remove any cellulose molecules. Thus, the reduction in intensity at 1162 cm^{-1} could be due to removing C—O—C symmetric stretching of hemicellulose only. As a result, the lower content in Xylan, Quinine, Quinine methides elements and adsorbed water in hemicellulose in hot alkali treated OPS compared to the untreated case indicates that hot alkali treatment was effective in removal some parts of the hemicellulose.

Thermal Behavior Study of OPS by Thermogravimetric Analysis

Effect of Different Treatment. Figure 9 illustrates the influence of washing treatment on the results of thermal analysis for OPS powder, i.e., not in the composite. It has been previously reported [3, 28, 29] that OPS, a cellulose based material, tends to degrade in three main stages according to the TGA/DTG curves as follows: (i) evaporation of moisture (35–155°C), (ii) hemicellulose degradation between 248 and 340°C (maximum at 288.7°C), and (iii) cellulose degradation between 345 and 400°C (maximum at 359.7°C). The effect of water and alkali treatment on the onset, endset, and peak positions of OPS powder have been presented in Table 4.

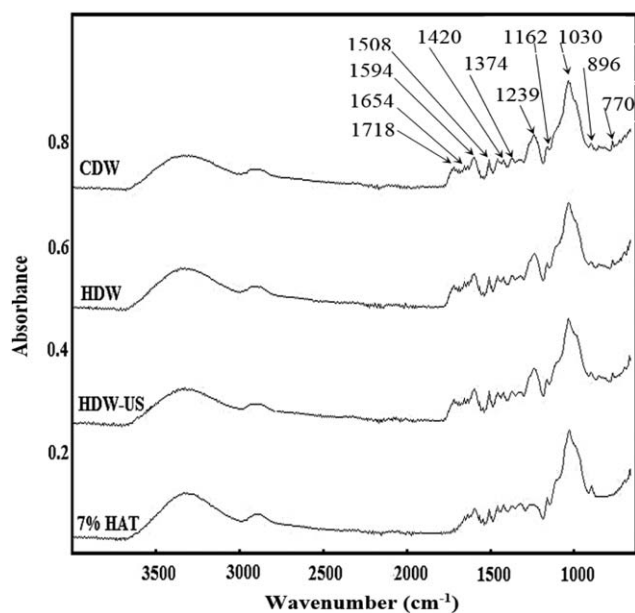


FIG. 8. FTIR spectra of untreated and treated OPS in different condition.

TABLE 3. Assignment of major absorption FTIR spectra peaks in untreated OPS

Wave number (cm ⁻¹)	Absorbance	Functional group	Assignment	Reference
896	0.115	C—H	C—O—C, C—C—O, and C—C—H deformation and stretching	[24]
1030	11.95	C—H and C—O	C—O stretch of primary alcohol, C—H stretch of Guaiacyl, aromatic C—H in plan deformation of lignin	[20, 25]
1162	0.319	C—O—C	C—O—C symmetric stretching of β(1,4)-glycosic linkage for cellulose I and II and hemicellulose	[23, 26]
1239	2.870	C—O	C—O syringyl ring and C—O stretch in lignin and Xylan (hemicellulose)	[20]
1374	0.270	C=O C—OH	Carbonyl band of xylan, the C—OH in plane stretching of cellulose and aliphatic C—H stretching in methyl and phenol OH	[19, 23, 27]
1420	0.125	C—H C—OH	C—H bending and OCH of crystalline cellulose	[19, 24]
1508	0.523	C=C	Aromatic ring (lignin), Guaiacyl, and Syringyl elements	[27]
1594	0.901	C=C	C=C stretching of aromatic ring (lignin)	[21]
1654	0.013	—OH C—H and C=O	—OH bending mode for the presence of water in hemicellulose and the C—H bending and C=O stretching frequency of Quinine and Quinine methides	[19, 23]
1718	0.223	C=O (—COOH)	Conjugated carbonyl groups of aldehydes and ketones and hydroxycinnamic acids (lignin)	[19, 21]

Lignin pyrolysis was believed to occur in the range of 160–900°C with an associated peak at 367°C which was obscured beneath the hemicellulose and cellulose peaks [30]. Thus, except for the case of HDW-US the lignin peak was not apparent in the DTG curves. Consequently,

lignin decomposition information was reported in two separate regions, i.e., first and second parts of lignin decomposition, as shown in Table 4. The step analyses of all samples based on the dry mass have been listed in Table 5. Note that the mass loss values of the hemicellulose or cellulose in Table 5 refer to the mass losses in hemicellulose or cellulose decomposition regions together with the main part of the lignin decomposition section. Therefore, the main region of lignin decomposition has been left out of Table 5 with only the first and second parts of the mass loss of lignin being presented.

It has been previously reported [3, 31] that the decrease in mass residue for washed natural filler is attributed to the removal of impurities and water-soluble polysaccharides present on the surface of the filler. In light of this, mass residue in the char yield may be an effective indicator of impurity removal due to washing. It should be noted that, for the nondegradable components, which remain as char yield, hot distilled water (HDW) decreased the char yield from 25.5% (for CDW) to 13.8% with the addition of sonication (HDW-US) reducing the char yield to only 2.29%. These results clearly indicate that, for the HDW-US OPS powder, the peak position shifted to a lower temperature with the temperature range (onset and endset) of decomposition for hemicellulose and cellulose being decreased significantly due to sonication as shown in Table 4. Consequently, due to the significant displacement of the hemicellulose (291–284°C) and cellulose (358–321°C) peaks in the HDW-US treated powder, a peak attributed to lignin decomposition was also apparent in the DTG curve which indicated a significant increase in mass loss (from 16.8% to 44.0%) in the second stage of lignin mass loss.

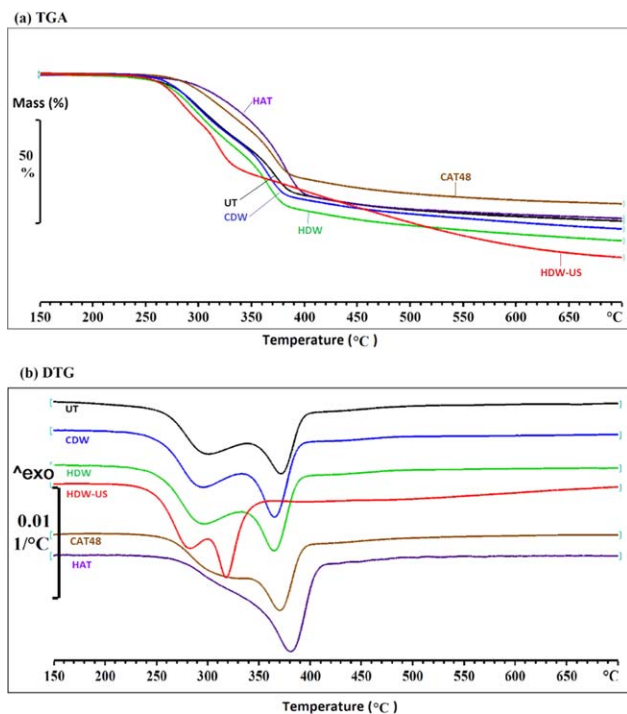


FIG. 9. Effect of water and alkali treatment on the thermal properties of OPS powder: (a) thermogravimetric analysis (DTA) and (b) derivative thermogravimetric (DTG) analysis. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

TABLE 4. Effect of water and alkali treatment on the onset, endset, and peak positions of OPS powder

Sample		UT	DW	HDW	HDW-US	CAT24	HAT24
Moisture evaporation	Onset (°C)	38.0	40.0	39.0	41.7	36.0	32.0
	Peak (°C)	69.0	61.0	63.0	71.6	90.0	68.0
	Endset (°C)	141	121	150	157	150	146
Lignin first part decomposition	Onset (°C)						
	Endset (°C)	244	263	246	252	249	251
Hemicellulose decomposition	Ondset (°C)						
	Peak (°C)	290	290	291	284	Partially removed	Almost removed
	Endset (°C)	327	334	326	310	333	330
Cellulose decomposition	Ondset (°C)						
	Peak (°C)	360	359	358	321	358	359
	Endset (°C)	382	382	381	370	381	390
Lignin second part decomposition	Ondset (°C)						
	Peak (°C)	a	a	a	395	a	a
	Endset (°C)	680	680	680	680	680	675

^aBeneath the hemicellulose and cellulose peaks.

In contrast to this, the peak attributed to hemicellulose decomposition was almost absent in the hot alkali treatment specimen (Fig. 9b) with this peak also being significantly reduced in the CAT1 specimen. The thermal analysis results also indicated that both the cold and hot alkali treatments reduced the mass loss attributed to hemicellulose decomposition when compared to the water treatments and thus increased the amount of cellulose present in the treated OPS powder. Looking at the results it was not clear how much of the hemicellulose or lignin had been removed (as a result of the various treatments) within the hemicellulose decomposition region during thermal analysis with this being attributed to the wide temperature range of lignin decomposition. It has previously been reported [32] that mass residues for the lignin, hemicellulose, and cellulose components are 42%, 9%, and 0.5%, respectively, which indicates that most of the char yield in natural filler is due to lignin. Consequently, the larger mass residue for the CAT48 treated powder (33.9%) compared to HAT (25.3%), together with the smaller mass drop in the second stage of lignin decomposition, appears to suggest that hot alkali treatment may be able to remove a portion of the lignin, together with the majority of the hemicellulose, which are difficult to thermally degrade under normal circumstances.

Effect of Alkali Concentration. Figure 10 illustrates the effect of NaOH concentration on the thermal properties of hot alkali treated OPS powder. Both the TGA (Fig. 10a) and DTG (Fig. 10b) data indicate that increasing the NaOH concentration up to 7% did not significantly change the thermal analysis features. However, further increasing the concentration to 9% produced thermal analysis curves indicative of a substantial change in the OPS structure. For example, the main DTG peak, which is attributed to cellulose decomposition, had its maximum shifted from 322°C for the 7% hot alkali treated OPS to 303°C for the 9% case. Subsequently, the 9% hot alkali specimen also exhibited a lignin decomposition peak between 393 and 626°C with a maximum at 478°C. The trend in these results is consistent with a previous study [8] that reported higher concentrations of alkali solution to have produced extensive damage in wood fibers in wood plastic composite (WPC).

The effect of NaOH concentration on the lignin mass loss and mass residue obtained from TGA curves for hot alkali treated OPS powder has been presented in Fig. 11. The data indicate a steady decline in mass residue and slight increase in lignin mass loss for increasing alkali concentrations up to 7%. However, the 9% alkali concentration OPS powder exhibited an additional substantial

TABLE 5. Effect of water and alkali treatment on the mass losses of OPS powder (dry based analysis)

Sample	Lignin mass loss		Hemicellulose Mass loss (%)	Cellulose Mass loss (%)	Char Mass residue (%)
	First stage (%)	Second stage (%)			
UT	3.21	13.0	29.9	25.2	28.7
DW	2.72	15.2	27.8	28.8	25.5
HDW	2.50	16.8	34.7	32.3	13.8
HDW-US	2.15	41.0	27.9	26.6	2.29
CAT48	1.23	13.4	26.3	25.2	33.9
HAT	2.14	11.1	23.0	38.4	25.3

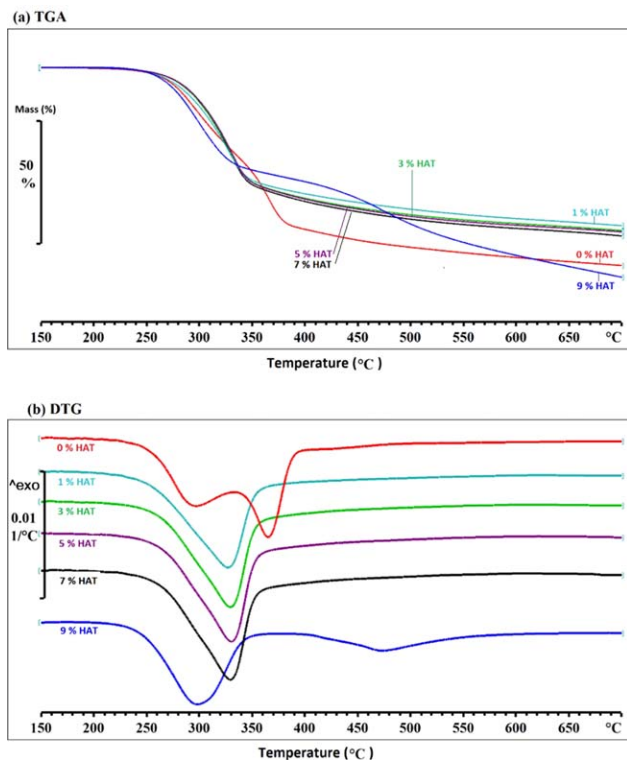


FIG. 10. Effect of sodium hydroxide (NaOH) concentration on the thermal properties of hot alkali treated (HAT) OPS powder: (a) thermogravimetric analysis (TGA) and (b) derivative thermogravimetric (DTG) analysis. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

increase in lignin mass loss combined with a significant decrease in mass residue.

From the above discussion (Figs. 3, 7, and 11), it can be concluded that the optimum concentration of hot alkali treatment required for maximum mechanical performance of natural filler reinforced polymer composites can be simply obtained from thermal analysis. In other words, the alkali concentration should be allowed to increase as far as possible while there is no significant change in TGA and DTG data. However, increasing the alkali con-

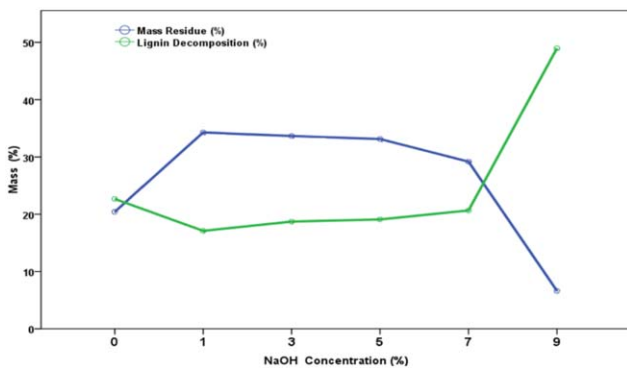


FIG. 11. Effect of sodium hydroxide (NaOH) concentration on the lignin mass loss and mass residue of hot alkali treated OPS powder. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

centration beyond the optimal value results in removal of some parts of the natural filler which results in a separation of phases between the lignin and cellulose components as reflected in Fig. 10. Likewise, Fig. 10 indicates that the lignin mass loss and the mass residue for natural filler started to dramatically change once the optimum alkali treatment conditions has been passed.

It is well known that, within natural fiber, lignin acts as a matrix phase while cellulose acts as the reinforcement phase whereas the role of hemicellulose is to bind the matrix and reinforcement together. However, should the treated fiber lose a portion of this binder (hemicellulose) due to the alkali concentration (9% in this case) being too high then phase separation occurs between the filler and matrix within the natural fiber as evident in Fig. 10. This is in good agreement with FTIR the results which indicated that the tight linkage of polysaccharides in the cell wall by ether linkages can be removed by HAT. In other words, further increases in alkali concentration beyond a certain point appear to deteriorate the structure of the natural filler which leads to poor mechanical performance of the natural filler and its resulting polymer composite. Previous research on the crystallinity of natural fibers [33] has indicated that alkali treatment leads to the removal of hydrogen bonds in the network structure of natural fiber with a subsequent decrease in the amount of crystalline cellulose due to its conversion to amorphous cellulose. Other research work [34] which investigated the effect of alkali treatment of rice husk particles reported that the asperities of the filler surface had eroded with higher concentrations of alkali solution. This effect had resulted in the generation of cracks on the rice husk particles which led to a decrease in the mechanical performance of the resulting polymer composite due to ineffective stress transfer between the matrix and fibers. It should be noted that, while the present study utilized a constant time and varying concentration, a similar effect would presumably be noted for the situation of a constant concentration and varying treatment time.

CONCLUSIONS

The thermal analysis of treated OPS powder from Palm Oil biomass and the mechanical performance of isophthalic unsaturated polyester composites reinforced with water and alkali treated OPS have been presented in this paper. The results of this study revealed that distilled water treatment significantly enhanced mechanical performance of the composites by improving the mechanical interlocking between the OPS powder and polymer matrix. The utilization of elevated temperature (90°C) was effective for both water and alkali treatment in order to further enhance mechanical performance of the composites with sonication in hot distilled water achieving the highest mechanical performance through the optimal removal of impurities, wax, and oily materials from the OPS powder surface.

Thermogravimetric analysis (TGA) of the OPS powder together with scanning electron microscopy indicated that the improvement in composite mechanical properties due to washing treatment could be attributed to increased surface roughness of the OPS powder generated by the removal of surface impurities, waxes, and lignin. Fourier transform infrared spectroscopy (FTIR) confirmed that Xylan, Quinine, Quinine methides elements, and adsorbed water were removed as the parts of hemicellulose. Moreover, Syringyl and Guaiacyl elements, aldehydes, and ketones and acetyl group in hydroxycinnamic acids associated with the alcoholic polysaccharides were also removed from lignin by hot water and hot alkali treatments. The optimum hot alkali concentration (7%) at 90°C for 1 h to enhance composite mechanical performance was found to be readily obtained from thermogravimetric analysis. For further increases in alkali concentration above this optimum amount, significant increases in lignin mass loss and decreases in mass residue were observed. It was concluded that, at excessively high alkali concentrations (and/or treatment times), hemicellulose, which acts as a binder for cellulose and lignin within natural fiber, is preferentially removed which causes a phase separation between the filler and matrix components of the natural fiber resulting in a deterioration of the fiber structure and subsequent poor composite mechanical performance.

REFERENCES

1. P. Shafiqh, M.Z. Jumaat, and H. Mahmud, *Int. J. Phys. Sci.*, **5**, 2127 (2010).
2. H.L. Chong, P.S. Chia, and M.N. Ahmad, *Bioresour. Technol.*, **130**, 181 (2013).
3. O. Nabinejad, D. Sujan, M.E. Rahman, and I.J. Davies, *Mater. Design*, **65**, 823 (2015).
4. A. Hassan, A.A. Salema, F.N. Ani, and A.A. Bakar, *Polym. Compos.*, **31**, 2079 (2010).
5. M.S. Sreekala, M.G. Kumaran, and S. Thomas, *J. Appl. Polym. Sci.*, **66**, 821 (1997).
6. L. Yan, N. Chouw, and K. Jayaraman, *Composites Part B*, **56**, 296 (2014).
7. A. le Duigou, A. Bourmaud, E. Balnois, P. Davies, and C. Baley, *Ind. Crops Prod.*, **39**, 31 (2012).
8. U.J. Alengaram, B.A.A. Muhit, and M.Z. Jumaat, *Construc. Build. Mater.*, **38**, 161 (2013).
9. S.P. Yap, U.J. Alengaram, and M.Z. Jumaat, *Mater. Design*, **49**, 1034 (2013).
10. Kim, J. and K. Pal, Springer, 'Surface Modifications in WPC with Pre-Treatment Methods', Recent Advances in the Processing of Wood-Plastic Composites, Berlin, 32, (2011).
11. A. Valadez-Gonzalez, J.M. Cervantes-Uc, R. Olayo, and P.J. Herrera-Franco, *Composites Part B*, **30**, 221 (1999).
12. X. Li, L. Tabil, and S. Panigrahi, *J. Polym. Environ.*, **15**, 25 (2007).
13. Y. Xie, C.A.S. Hill, Z. Xiao, H. Militz, and C. Mai, *Composites Part A*, **41**, 806 (2010).
14. M.J. John and R.D. Anandjiwala, *Polym. Compos.*, **29**, 187 (2008).
15. O. Nabinejad, D. Sujan, M. Rahman, M. Reddy, W.Y. Liew, and I.J. Davies, *Adv. Mat. Res.*, **980**, 86 (2014).
16. M.A. Fuqua, S. Huo, and C.A. Ulven, *Polym. Rev.*, **52**, 259 (2012).
17. H.M. Akil, M.F. Omar, A.A.M. Mazuki, S. Safiee, Z.A.M. Ishak, and A. Abu Bakar, *Mater. Design*, **32**, 4107 (2011).
18. M. John and S. Thomas, *Carbohydr. Polym.*, **71**, 343 (2008).
19. M.M. Kabir, H. Wang, K.T. Lau, and F. Cardona, *Appl. Surf. Sci.*, **276**, 13 (2013).
20. K.K. Pandey and A.J. Pitman, *Int. Biodeter. Biodegrad.*, **52**, 151 (2003).
21. R. Hoseinzadeh Hesas, A. Arami-Niya, W.M.A. Wan Daud, and J.N. Sahu, *J. Anal. Appl. Pyrol.*, **104**, 176 (2013).
22. Koch, G., 'Raw Material for Pulp', Handbook of Pulp, H. Sixta, Ed., Wiley-VCH Verlag GmbH, Weinheim, Germany, 21 (2008).
23. Xu, G. Wang, L. Liu, and J. Wu, *J. Appl. Surf. Sci.*, **280**, 1 (2013).
24. D. Dai and M. Fan, *Mater. Sci. Appl.*, **1**, 336 (2010).
25. E. Sinha and S.K. Rout, *Bull. Mater. Sci.*, **32**, 65 (2009).
26. W. Zhou, D. Zhu, A. Langdon, L. Li, S. Liao, and L. Tan, *Bioresour. Technol.*, **100**, 4919 (2009).
27. J. Shi, D. Xing, and J. Lia, *Energy Procedia*, **16**, 758 (2012).
28. P. Methacanon, U. Weerawatsophon, N. Sumransin, C. Praharn, and D.T. Bergado, *Carbohydr. Polym.*, **82**, 1090 (2010).
29. O. Nabinejad, D. Sujan, M.E. Rahman, and I.J. Davies, *J. Therm. Anal. Calorim.*, **122**, 227 (2015).
30. N.P.G. Suardana, M.S. Ku, and J.K. Lim, *Mater. Design*, **32**, 1990 (2011).
31. P.M. Stefani, D. Garcia, J. Lopez, and A. Jimenez, *J. Therm. Anal. Calorim.*, **81**, 315 (2005).
32. A.R. Martin, M.A. Martins, O.R.R.F. da Silva, and L.H.C. Mattoso, *Thermochim. Acta*, **506**, 14 (2010).
33. S. Kalia, B.S. Kaith, and I. Kaur, *Polym. Eng. Sci.*, **49**, 1253 (2009).
34. B.S. Ndazi, S. Karlsson, J.V. Tesha, and C.W. Nyahumwa, *Composites Part A*, **38**, 925 (2007).