MORPHOLOGICAL, SPECTROSCOPIC, AND THERMAL PROPERTIES OF ALKALI-TREATED AND CHEMICALLY MODIFIED OIL PALM EMPTY FRUIT BUNCH FIBERS AND OIL PALM FROND FIBERS: A COMPARATIVE STUDY

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The effect on morphological, spectroscopic, and thermal properties of oil palm empty fruit bunch fibers (OPEFB fibers) and oil palm frond fibers (OPF fibers) following treatment and modification with sodium hydroxide and succinic anhydride, respectively, were investigated. The evidence of treatment was observed by weight gain and FT-IR. The effect of the treatment upon the fiber surfaces was examined using scanning electron microscopy (SEM), which indicated that succinic anhydride treatment led to smoother surfaces as compared to the sodium hydroxide. The thermal degradation was carried out by thermal gravimetric analysis, which exhibited a different degree of mass loss due to different treatments.

Keywords: Succinic anhydride; OPEFB fibers; OPF fibers; SEM, FT-IR, TGA/DTG

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INTRODUCTION

Natural fibers are attracting attention from scientists and technologists currently due to environmental concerns. Plant fibers such as jute, pineapple leaf, sisal, flax, hemp, kenaf, etc., have been used to commercialize a range of products obtained from them (Hassan et al. 2010). The natural fibers have been used to replace various inorganic fibers (glass, aramid, and carbon) with a goal of causing less environmental damage. Malaysia is among the greatest producers of raw natural fibers from oil palm mills, and presently large proportions of these raw fibers are recycled and are used as fertilizers. But due to other environmental problems, for example production of ash, which involves emission of white smoke, it is necessary to consider other uses of these biomass resources (Soom *et al.* 2006). Using natural fibers as a source of energy, some mills have tried to utilize them as a fuel by reducing their moisture content. In addition making high-end products from natural fibers affecting positively to the financial conditions of common people have led to new economical strategies in order to generate new revenues. However, some drawbacks of natural fibers such as increased moisture absorption, low thermal stability, and limited mechanical strength have led to undesirable results in production value ended products (Abdul Khalil and Rozman 2004; Abdul Khalil *et al.* 2009).

Oil palm empty fruit bunch fibers have been treated as waste after the extraction of oil from fruits and nuts (Law *et al*. 2007). The average yield of OPEFB fiber is about

400 g per bunch (Sreekala *et al.* 1997). In fact, with the increasing of the oil palm plantation, the amounts of the OPEFB fibers have also gradually increased. Hence, the vast quantity of the OPEFB fibers and other agricultural wastes have posed a serious threat to our environment. Oil palm fibers also are hygroscopic, which will lead to changes in dimensional and mechanical properties. Furthermore, after extraction when fibers are exposed to the moisture, they are easily attacked by decay organisms. For this reason, oil palm fibers are subjected to various types of modification process to improve the decay and moisture resistance (Abdul Khalil *et al*. 2007). Therefore, we herein report chemical modification and base treatment of OPF fibers and OPEFB fibers to evaluate the effects on fundamental properties in order to compare whether alkali treatment or chemical modification by succinic anhydride leads to enhanced properties.

EXPERIMENTAL

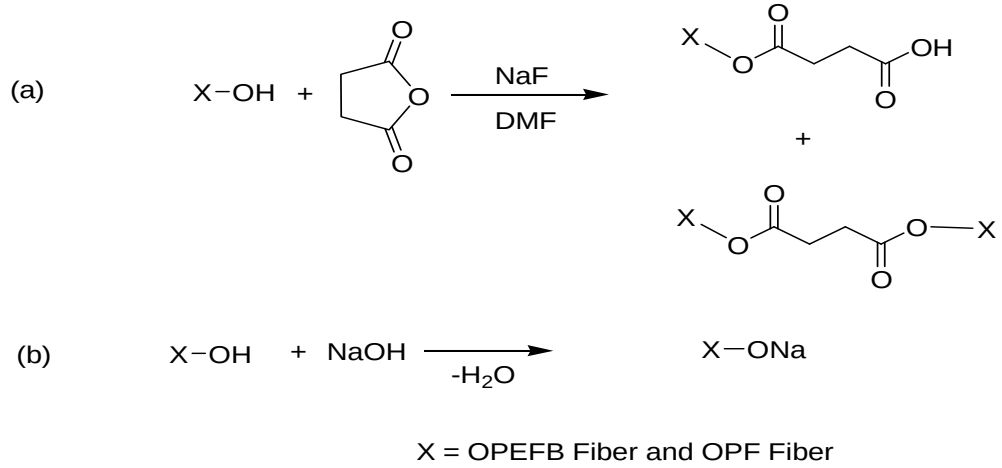
Materials and Procedures

OPF fibers and OPEFB fibers used in this research were collected from a local plantation source, Nibong Tebal Paper Mills (NTPM), Seberang Prai, Penang, Malaysia. Succinic anhydride, sodium formate, N,N- dimethylformamide, and NaOH platelets were purchased from Sigma-Aldrich (Malaysia). Acetone (LR grade) and acetic acid were procured from Sigma-Aldrich (Malaysia) and were used further purification.

Chemical Modification Using Succinic Anhydride

The alkali treatment and chemical modification (Scheme 1) (Bhat *et al.* 2010)were carried accordingly to our earlier methods, which are described below.

The succinic anhydride in dimethyl formamide (150 mL) and its catalyst, sodium formate (NaF), were used with the ratio of 10:1 for modification of OPEFB fibers and OPF fibers. The process was carried out at 100 ^{o}C for 3 hours. After the modification process, the samples were washed rigorously by acetone to clean up any remaining acid. The samples were air dried for a few hours before being oven-dried for 24 hours with a temperature of 60°C.



Scheme 1. Representation of modification and alkali-treated OPEFB fibers and OPF fibers

Alkaline Treatment

Fresh solutions of 5% NaOH were prepared; the samples were immersed for 24 hours, as this is the optimum condition for alkaline treatment. After the 24 hours, the samples were taken out and cleaned by using 1% acetic acid solution and washed several times with distilled water to remove chemical residue carried by the material. The samples were air dried for few hours before being kept for drying in an oven at 60 ^{o}C for 24 hours.

Scanning Electron Surface Microscopy (SEM)

The effect of the modification on the fiber surface morphology was examined using Scanning Electron Microscopy (Leo Supra 50 VP, Carl-Ziess SMT, Germany SEM). The samples were cut into about 3 mm x 3 mm pieces. Before being coated with gold, the samples were placed into a pre-vacuum process to apply a thin coating. The gold coating was about 20 nm to ensure the good conductivity for the analysis.

Fourier-Transform Infrared (FT-IR)

The Fourier-transform infrared (FT-IR) was carried out AVATAR 360 FT-IR Spectrometer. The samples were mixed with potassium bromide (KBr), and the mixture was then pressed into pellets. The spectrum was recorded from 4000 cm^{-1} to 400 cm^{-1}.

Thermal Gravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was carried out with a Perkin Elmer TGA 6 Thermogravimetric Analyzer at the heating rate of 20 ^{o}C/min under nitrogen gas. In the testing, samples were ground into powder form, then placing the sample into the sample pan (usually made from platinum). The range of the temperature was employed from 30 ^{o}C to 800 ^{o}C.

RESULTS AND DISCUSSION

Weight percent of the oil palm frond fibers and oil palm empty fruit bunch fibers increased after treatment with succinic anhydride (SA). The weight of oil palm frond fibers increased by about 17.5% and the oil palm empty fruit bunch increased only 15.5%. These results gave evidence of an esterification process linking the SA to fibers in the form of diesters (Doczekalska *et al.* 2007). However, after alkaline treatment, both samples showed the decrease in the weight percent gain. The was 6.8% and 5.4% for oil palm frond fibers and oil palm empty fruit bunch fibers, respectively. The weight loss can be attributed to the loss of various chemical constituents into smaller fragments.

Scanning Electron Microscope Analysis (SEM)

The surface morphology of the untreated OPEFB fibers is given in Fig. 1a, which shows some pores on the fiber surface, which became more prominent on the surface of the fiber after alkali treatment (Sreekala *et al.* 1997), and the surface became degraded (Fig. 1b). However, some silica still remained on the surface. After being treated with SA (Figure 1c), it is apparent that the surfaces of the fiber had become cleaner, and the roughness had been reduced.

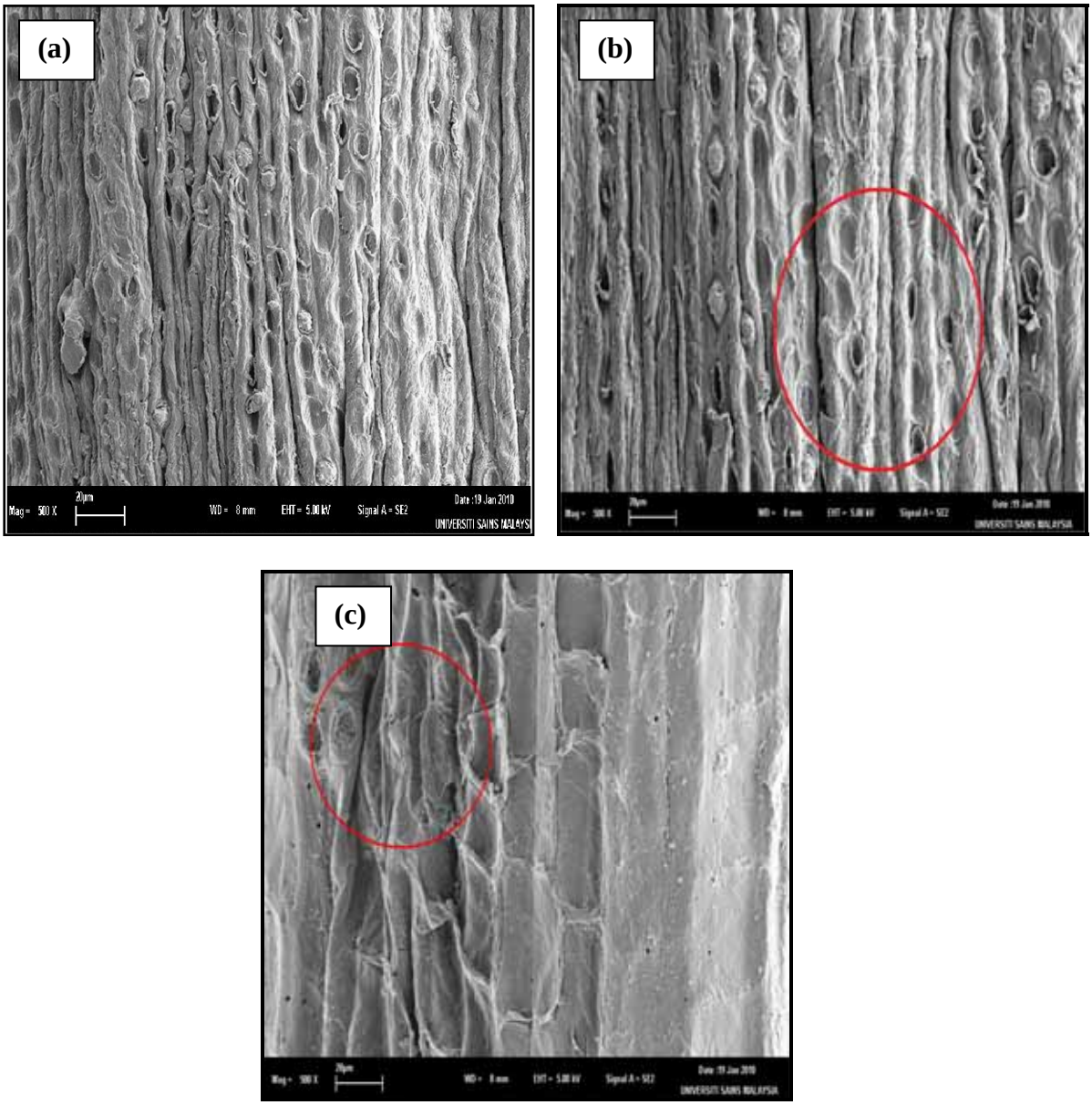


Fig. 1. a) Untreated OPEFB fiber, b) OPEFB fiber treated with NaOH, and c) OPEFB fiber treated with SA of SEM micrograph under 500x magnification

After treatment with SA (Fig. 1c), the surfaces of the fiber had become cleaner, and the roughness was reduced. The surface of the OPF fiber had differences in roughness and smoothness. The untreated OPF fiber surface was full of impurities, and the surface was very rough. Figure 2 (b) shows evidence of degradation of the surface following treatment with the alkali, which is apparent due to the changed morphology. After treatment with SA (Fig. 2c) the fiber was cleaner, and the surface also had become smoother. Besides that, the silica on the surface can be clearly seen.

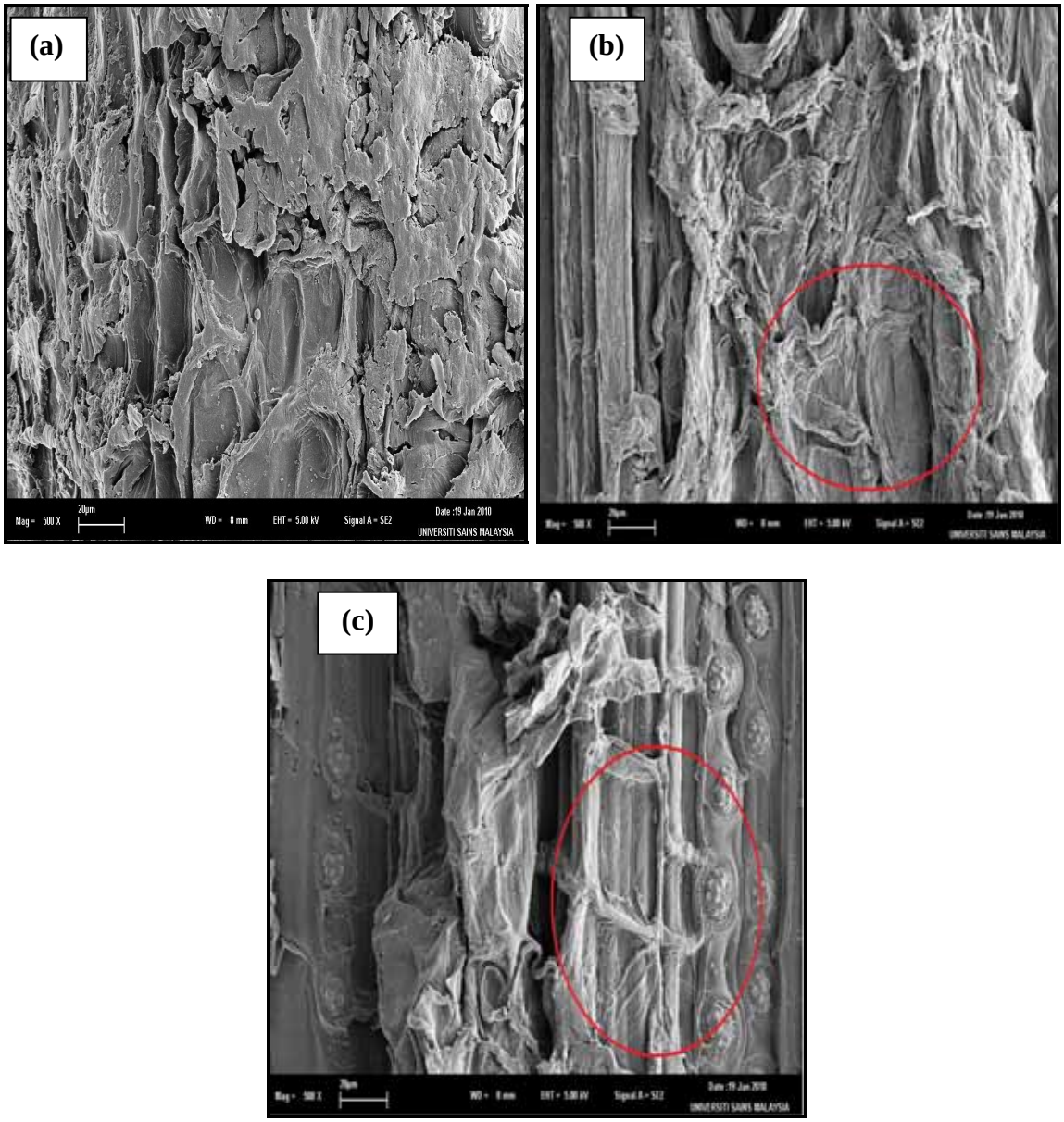


Fig. 2. a) Untreated OPF fiber, b) OPF fiber treated with NaOH, and c) OPF fiber treated with SA of SEM micrograph under 500x magnification

Fourier Transform Infrared Studies

The FT-IR spectra of untreated and treated OPEFB and OPF fibers, by alkali and succinic anhydride, are given in Figs. 3 and 4. The untreated OPEFB fibers and OPF fibers exhibited a broad and intense absorption band at 3413 cm^{-1} and 3419 cm^{-1}, respectively, and were assigned to the O-H stretching vibration of cellulose, hemicelluloses, and lignin components of OPEFB fibers and OPF fibers.

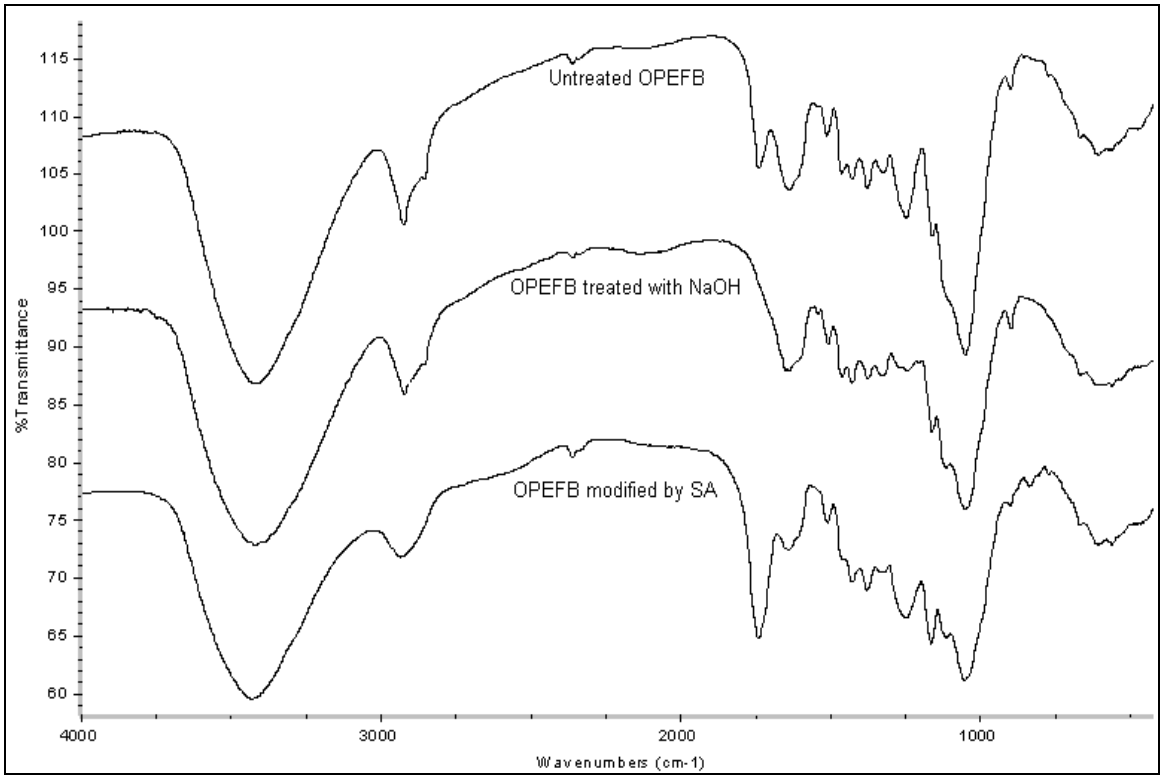


Fig 3. FT-IR Spectra of untreated OPEFB fiber, and OPEFB fiber treated with NaOH or SA

In FT-IR spectra of OPEFB fibers, a shift of 10 cm^{-1} was observed for O-H stretching in the case samples modified by succinic anhdydride; however, broadening with a slight shift of O-H stretching vibration by treatment of NaOH was obtained. The broadening of O-H stretching vibration can be attributed to hydrogen bonding between different functionalities.

The absorption bands at 2922 cm^{-1} in untreated and treated OPEFB fibers were due to the stretching vibration of the CH_2 moiety of methyl, methylene, and methoxy groups (El-Meligy *et al.* 2004). The medium intensity band in untreated OPEFB fibers and OPF fibers, due to C=O stretching vibration appeared at 1736 cm^{-1} and 1733 cm^{-1}. These bands disappeared in alkali treated fibers; however strong and intense bands at 1739 cm^{-1} and 1732 cm^{-1} were observed in OPEFB fibers and OPF fibers, and can be assigned to the carbonyl functionality of succinic anhydride. The bands observed at 1511 cm^{-1} 1514 cm^{-1} in untreated OPEFB fibers and OPF fibers were assigned C=C aromatic stretching vibrations.

The C=C stretching vibration in succinic anhydride and alkali treated OPEFB fiber and OFB fiber were found at 1506 cm^{-1} and 1509 cm^{-1}, and 1505 cm^{-1} and 1508 cm^{-1}, respectively (Samal *et al.* 2001)

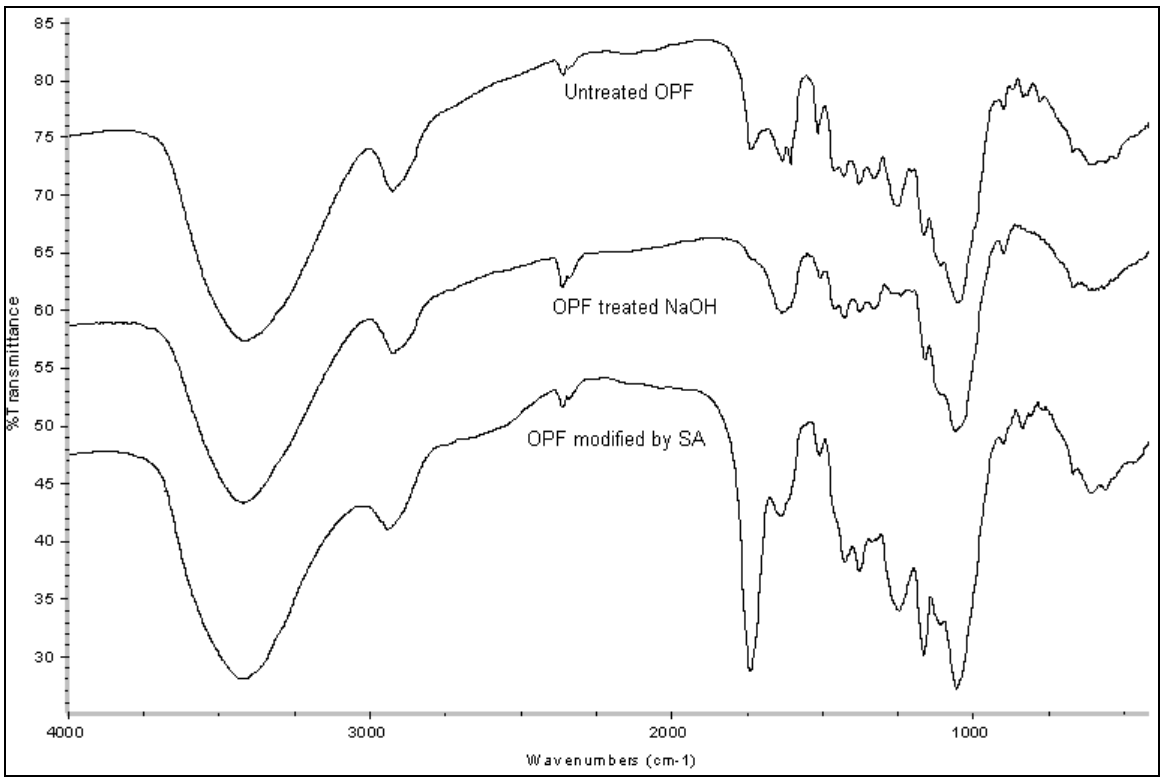


Fig. 4. FT-IR Spectra of untreated OPF fiber, and OPF fiber treated with NaOH or SA

The bands observed at 1636 cm^{-1} and 1633 cm^{-1} in untreated OPEFB fibers and OPF fibers were assigned to $\nu(H_2O)$ stretching vibrations due absorbed water. In succinic anhydride and alkali-treated OPEFB fiber and OFB fiber these bands were observed at 1639 cm^{-1} and 1638 cm^{-1}, and 1636 cm^{-1} and 1634 cm^{-1}, respectively, In addition, other assignments are presented in Table 1.

Table 1. FT-IR Spectral Data of Untreated and Modified OPEFB and OPF Fibers

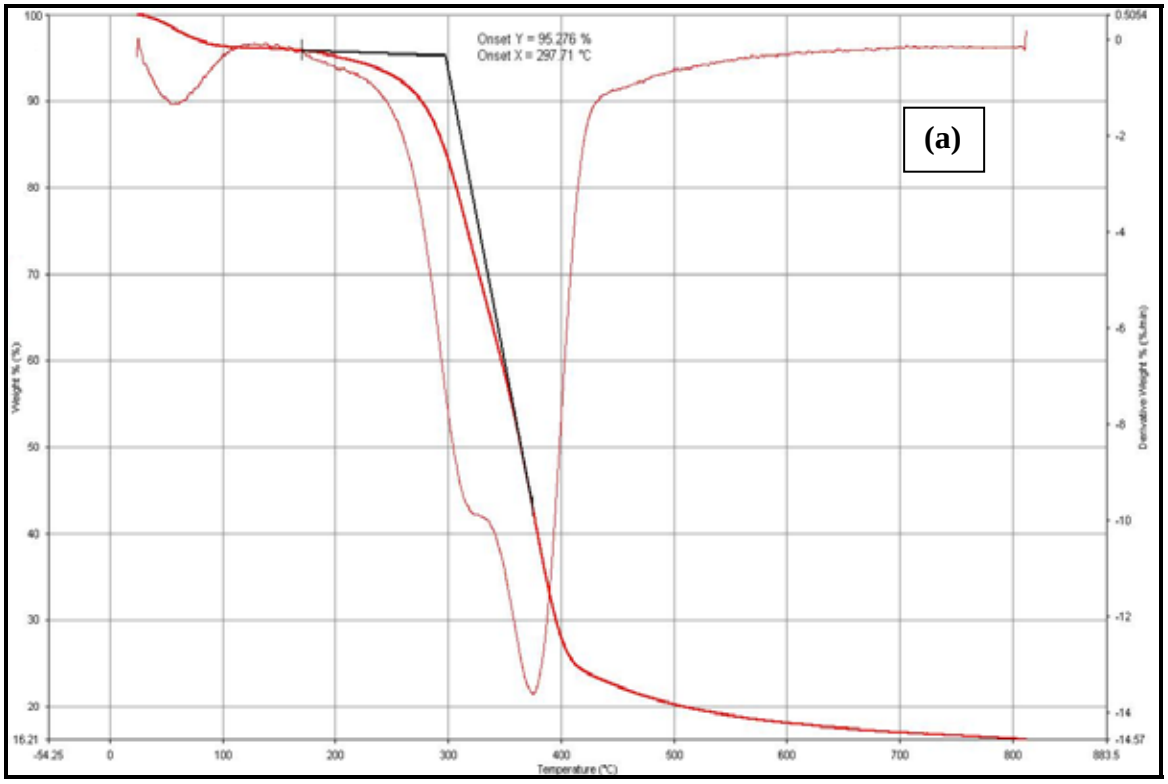
Sample	Untreated	NaOH	SA	Assignment
OPEFB	1461 cm^{-1}	1460 cm^{-1}	1461 cm^{-1}	-CH_2 bending glucopyranose
OPF	1462 cm^{-1}	1460 cm^{-1}	merged band	
OPEFB	1425 cm^{-1}	1424 cm^{-1}	1425 cm^{-1}	O-H in plane bending vibration
OPF	1426 cm^{-1}	1425 cm^{-1}	1423 cm^{-1}	
OPEFB	1376 cm^{-1}	1374 cm^{-1}	1377 cm^{-1}	C-H aliphatic bending vibration
OPF	1376 cm^{-1}	1374 cm^{-1}	1376 cm^{-1}	
OPEFB	1324-1245 cm^{-1}	1322-1240 cm^{-1}	1324-1245 cm^{-1}	Interaction between O-H bending and C-O stretching
OPF	1329-1250 cm^{-1}	1330-1236 cm^{-1}	1328-1243 cm^{-1}	
OPEFB	1160 cm^{-1}	1160 cm^{-1}	1163 cm^{-1}	-C-O-C- asymmetric stretching
OPF	1163 cm^{-1}	1159 cm^{-1}	1163 cm^{-1}	

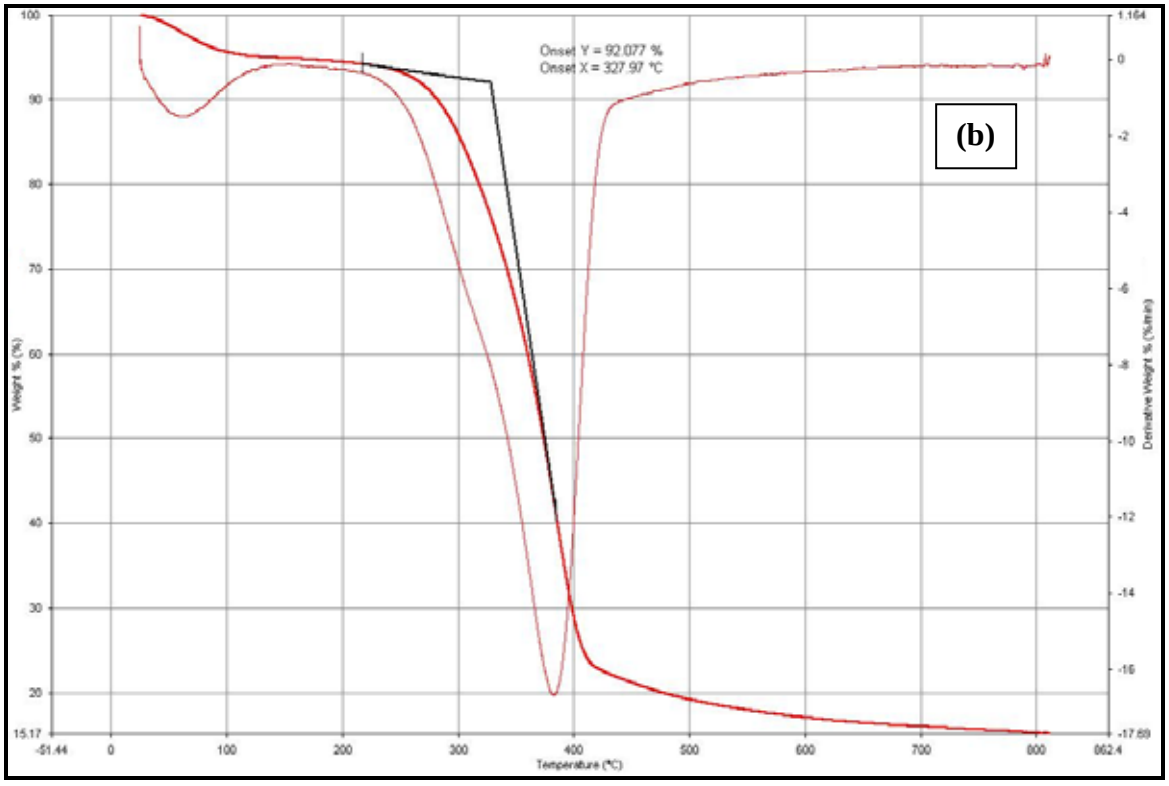
Thermal Analysis (TGA and DTG)

Thermograms including derivative curves of OPEFB and OPF fibers, untreated and treated, by NaOH and succinic anhydride, respectively, are given in Figs. 5 and 6. Figure 5 (a-c) shows similarities in the TGA curves exhibiting three stages of thermal degradation corresponding to loss of moisture content, volatile compounds, and carbohydrate polymers. The thermogram of untreated and treated OPEFB exhibited the first peak near 100 ^{o}C, corresponding to loss of moisture content. The second peak of degradation in temperature range from 195 to 360 ^{o}C was attributed to the degradation of cellulosic substances such as hemicellulose and cellulose (Threepopnatkul *et al*. 2009). The third peak was attributed to oxidation at higher temperatures. After careful observation of the derivative curve of the OPEFB treated with alkali, it was observed that three peaks were obtained, one among them in the temperature range of 280 ^{o}C to 310 ^{o}C being of weak intensity. The unusual trend obtained can be attributed to the structural changes in the cellulose backbone of fibers due to base (alkaline) hydrolysis. In the derivative curve of SA-treated OPEFB clear three-stage degradation was observed. At the end of the testing, char or black carbonaceous residue was left behind. The char formation is due to the lignin component in the samples. The decomposition of the lignin takes place within a broad range of temperature between 200 ^{o}C and 500 ^{o}C (Manfredi *et al*. 2006). Different patterns of percentage of weight losses were observed. Furthermore, it was observed that weight loss of 95.30% had occurred at 297.71 ^{o}C for untreated samples, whereas OPEFB treated with SA experienced a weight loss of about 95.68% and 50.36 % at 240.94 ^{o}C, respectively. The alkaline treated OPEFB fibers showed only a thermal degradation peak at 327 ^{o}C. This indicates that the point of thermal degradation had increased by about 30 ^{o}C, and the mass loss was attributed to cellulose degradation occurring in the sample.

The thermograms of untreated and treated OPF fibers are depicted in Fig. 6 (a-c). A similar observation of three-step degradation was observed, as in the case of alkali-treated OPF fibers, with weak peaks. According to Rosa *et al*. (2009), dehydration and evaporation of water occur at room temperature to 150 ^{o}C. For the untreated OPF fibers, the second stage of thermal degradation occurred with a weight percent loss of 93.62% at 185.45 ^{o}C. The OPF fibers treated with SA showed 96.70% weight percentage loss at 222.28 ^{o}C. Both degradations are attributed to the degradation of hemicelluloses (Threepopnatkul *et al*. 2009; Rosa *et al*. 2009). However, for NaOH-treated OPF fibers, no results showed degradation around this range. This is because hemicellulose has been hydrolyzed during the mercerization. The cellulose degradation of the untreated sample occurred at 306.20 ^{o}C with respect to weight loss 70.11%. For the OPF fibers treated SA, the degradation occurred at 360.23 ^{o}C with 48.11% weight loss.

As compared to the untreated OPF fibers, SA-treated OPF fibers exhibited increased degradation at about 55 ^{o}C. However, alkaline-treated OPF fibers thermal degradation occurred at 93.20% and 313.94 ^{o}C. There was only a slight increase in this after the treatment. Therefore, it is concluded from the thermograms that thermal stability varies with different treatments, which entirely depends on the nature and interaction of fiber and the reacting molecules.


Onset Y = 95.276 %
Onset X = 297.71 °C
(a)
Weight % (%)
Derivative Weight % (%/min)
Temperature (°C)


Onset Y = 92.077 %
Onset X = 327.97 °C
(b)
Weight % (%)
Derivative Weight % (%/min)
Temperature (°C)

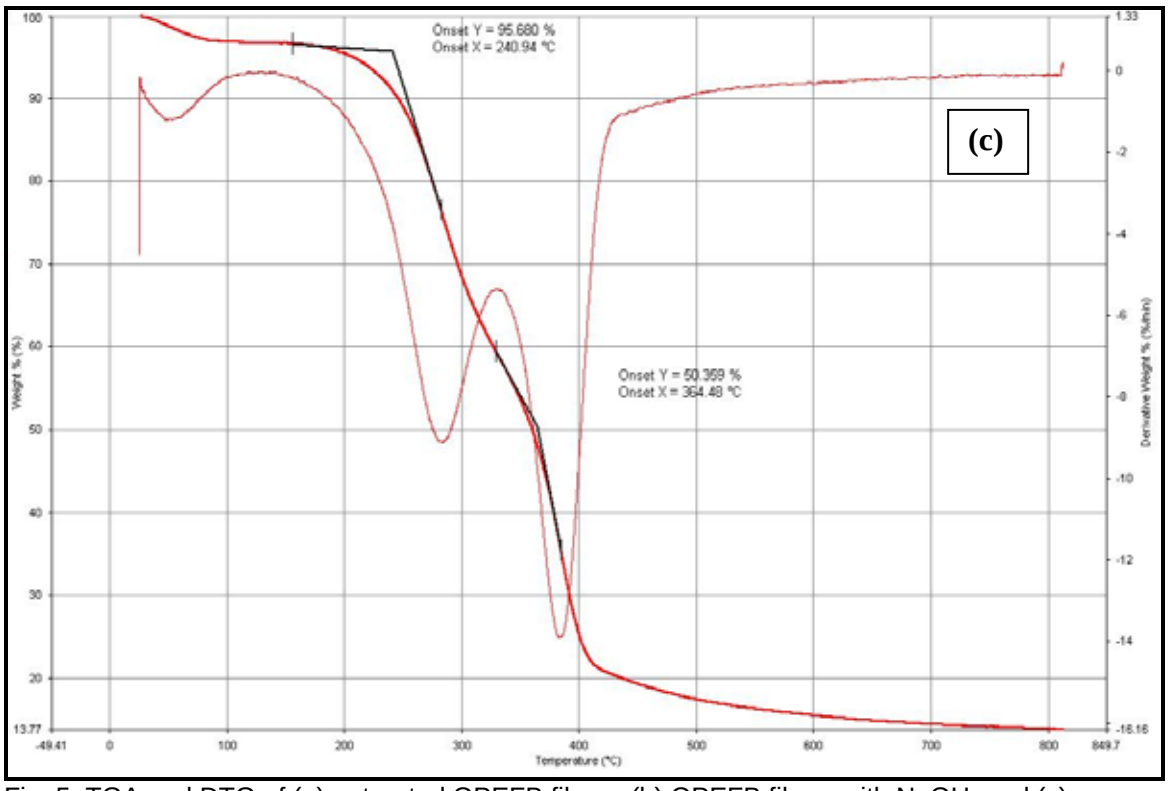
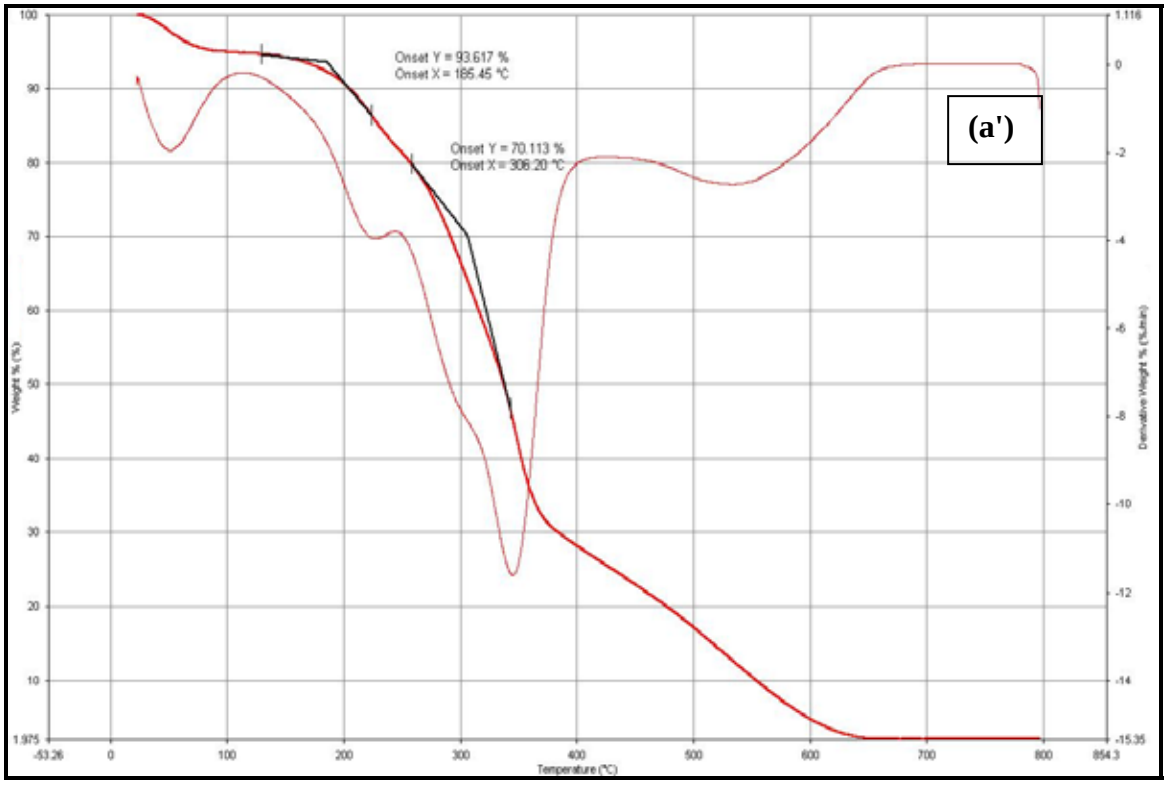


Fig. 5. TGA and DTG of (a) untreated OPEFB fibers, (b) OPEFB fibers with NaOH, and (c) OPEFB fibers treated with SA



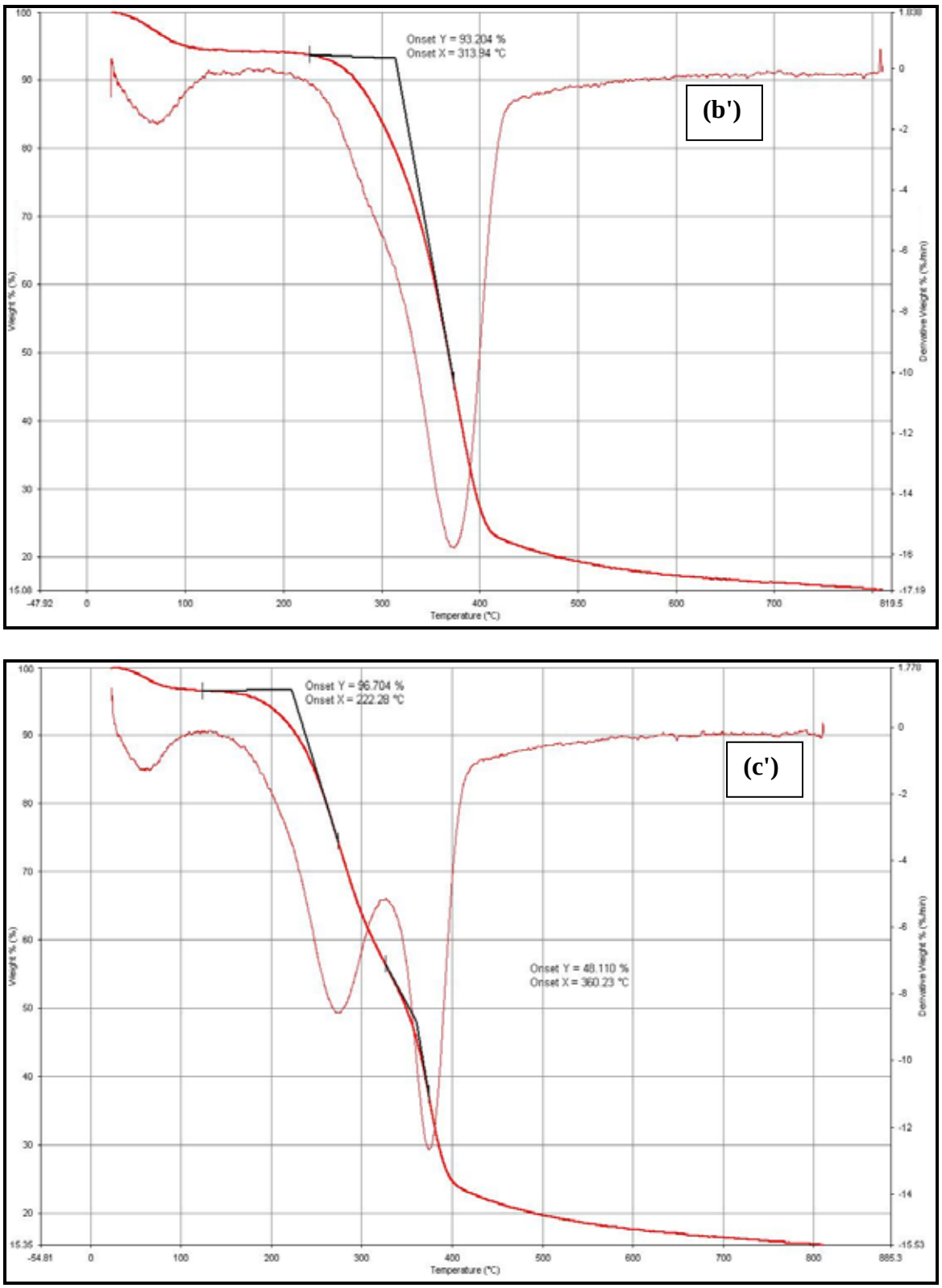


Fig. 6. TGA and DTG of (a') untretaed oil palm frond fibers, (b') oil palm frond fibers treated with NaOH, and (c') oil palm frond fibers treated with SA.

CONCLUSIONS

1. The treatment of OPEFB fibers and OPF fibers by sodium hydroxide and succinic anhydride effectively led to spectroscopic, morphological, and thermal changes.
2. FT-IR revealed changes in functional groups such as OH and carbonyl groups.
3. Significant differences in morphology were observed between treated and untreated fibers.
4. TGA and DTG curves also indicated differences in the thermal stability of treated and untreated OPEFB fibers and OPF fibers.
5. Treatment and modification of OPEFB fibers and OPF fibers by alkali and succinic acid will increase the availability of functional groups to interact strongly with matrix polymers to get better interfacial bonding; this approach can be explored in composite sciences.

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