Thermal Properties of Alkali-Treated Sugar Palm Fibre Reinforced High Impact Polystyrene Composites

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ABSTRACT

Thermal characterization of sugar palm fibre (SPF), reinforced high impact polystyrene (HIPS) composites, was studied by means of thermogravimetric analysis. The effects of alkaline treatment and compatibilizing agent on the thermal stability of the composites were evaluated. Alkaline treatment was carried out by soaking the fibres in 4 and 6% of NaOH solution, while treatment with compatibilizing agent was employed by adding 2 and 3% maleic anhydride-graft-polystyrene (MA-g-PS) to the composites. Both the treatments were aimed to improve the mechanical performance of the composites. From the study, the thermal stability of the treated composites was found to be higher than that of untreated composites. It is shown that the incorporation of sugar palm fibre influences the degree of thermal stability of the composites. The treatments on composites also contributed to shifting the peak temperature of degradation of the composites. In other words, there are strong chemical reactions between the components of the treated composites. The thermal stability of the composites, with alkaline treatment and compatibilizing agent, was found to be better as compared to those of the untreated composites.

Keywords: Thermal stability, sugar palm fibre, high impact polystyrene, thermogravimetry

INTRODUCTION

The application of natural fibres in the production of thermoplastic composites is highly beneficial as these materials have been shown to improve toughness, stiffness and strength of plastic. Moreover, these materials are cheap, biodegradable and also flexible. As

a substitute for glass fibre materials, they also reduce the wear of machinery. They are of low density and produce environmentally friendly goods (Bledzki & Gassan, 1999; George *et al*., 2001). Various types of natural fibres have been widely recognized in the study of reinforcement of thermoplastics such as sisal, abaca, kenaf, sugar palm, pineapple leaf, jute, flax, hemp, and sugarcane fibres (John & Thomas, 2008; Bledzki *et al*., 2007; Malkapuram *et al*., 2009; Joffe & Andersons, 2008).

Although natural fibre based reinforcement of thermoplastics has shown satisfactory results in some aspects, there are still problems at the interface between the fibre and matrix. They are not fully integrated due to the fact that natural fibres are hydrophilic and thermoplastics are hydrophobic. This caused poor adhesion, and thereby, stress is not fully transferred at the interface when loading takes place onto the material. In order to overcome this drawback, some treatments were usually applied. Mercerization was one famous treatment on the surface of natural fibres. Many studies by researchers everywhere have been reported on the improvement on the mechanical properties of the natural fibre composites after mercerization or alkaline treatment (Li *et al*., 2007). Another common treatment used to enhance the performance of natural fibre composites was the application of a compatibilizing agent such as maleic-anhydride to the thermoplastics matrix. The difference of this with that of the alkaline treatment is that maleic anhydride is not only used to modify the surface of fibre but also the thermoplastic matrix so as to achieve better interfacial bonding and mechanical properties in composites (Joseph *et al*., 2003). Meanwhile, dispersion of the fibres in polymer matrix was enhanced by this compatibilizing agent, and it also improved the quality of interfacial interaction that promoted adhesion of fibres and polymeric matrix.

Recently, the authors reported on the tensile properties (Bachtiar *et al*., 2011) of short sugar palm fibre reinforced high impact polystyrene composites. However, no work has reported on the thermal properties of these composites. Thermal analysis is an important analytical method in understanding the structure–property relationships and thermal stability of composite materials. Thermal analysis can be used to determine moisture content and volatile component present in composites. Since moisture content and volatile components have deteriorating effects on the properties of the composite, these studies are of great importance. Thermogravimetric (TG) analysis is one of the common methods used in assessing thermal properties of polymeric materials. The data indicate a number of stages of thermal breakdown, weight loss of the material in each stage and threshold temperature. Both TG and derivative thermogravimetry (DTG) provide information about the degree of degradation of the material (Joseph *et al*., 2003).

In the present paper, the results report on the present studies on the thermal properties of short sugar palm fibre reinforced high impact polystyrene composites under TG analysis after alkaline treatment and treatment with compatibilizing agent. The objective of the study was to look at the effects of the alkaline treatment and compatibilizing agent on the thermal stability of the composites.

MATERIALS AND METHOD

Materials

The high impact polystyrene (HIPS) used as the matrix polymer was Idemitsu PS HT 50, supplied by the Petrochemical (M) Sdn. Bhd., Pasir Gudang, Johor, Malaysia. The sugar palm fibre (SPF) was obtained from a traditional market in Aceh, Indonesia. The fibres were crushed with a pulverisette machine for shortening and sieved through 30 and 50 mesh screens. There were two types of treatment used in this study: (1) mercerization using an alkali solution and (2) polystyrene-block-poly(ethylene-ran-butylene)-block-poly(styrene-graft-maleic-anhydride) which was as a compatibilizing agent. NaOH and the MA-g-PS compatibilizing agent were supplied by Aldrich Chemical Company, Malaysia.

Treatment Processing

The first treatment was mercerization or alkali treatment. It was carried out by immersing the short fibres in NaOH solution for 1 hour at room temperature. Four and 6% NaOH were used as soaking solutions for the modification of the surface of the fibres. The fibre/solution ratio used was 1:20 (w/v). The treated fibres were then washed with distilled water to remove residual NaOH thoroughly. The drying process of the fibres was done using an oven at 100°C for 2 days. The second treatment included applying two different weight concentrations (2 and 3 wt. %) of the compatibilizing agent.

Composite Processing

The sugar palm fibres (40 wt. %) were mixed with the HIPS matrix using a common method as previously reported (Bachtiar *et al.*, 2011). The HIPS (58 wt. % and 57 wt. %) and compatibilizing agent (2 wt. % and 3 wt. %) were first premixed at room temperature for 3 minutes. The HIPS and the compatibilizing agent were then placed in a mixing chamber for about 2 minutes at 50 rpm, followed by the addition of the SPF for another 10 min. of mixing. The resulting material was then compressed in the mould using a Carver laboratory press with a metal frame size of 150 mm x 150 mm x 1mm at 100 bars and 165°C of temperature. Thereafter, it was subjected to a process of pre-heating for 5 minutes and full press-heating for 5 minutes. The processing pressure is 100 kg/cm². This was followed by cooling for 5 minutes using circulated water in a temperature of 20°C, and the final resulting composite was formed into sheets. The same technique was also applied for the alkali-treated sugar palm fibres, with a mixing composition of 40 wt. % alkali-treated fibre and 60 wt. % HIPS matrix.

Thermogravimetric Analysis

Thermogravimetric (TG) analysis is a common method used in understanding the relationship between the structure-property and thermal stability of composite materials. This testing was carried out on the specimens to calculate the degradability of weight in relation to change in the temperature. A TGA/SDTA 851ᵉ Mettler Toledo device was used. The specimens were observed from 30 to 600°C at a heating rate of 20 deg. C/min. and the nitrogen gas flow was 50 mL min. The weight of the samples varied from 6 mg to 20 mg.

RESULTS AND DISCUSSION

The TG analysis of sugar palm fibre, HIPS polymeric matrix, untreated SPF-HIPS composites and treated SPF-HIPS composites were studied as a function of % weight loss with the increase in temperature. Fig.1 and Fig.2 show the TG and Derivative TG curves of sugar palm fibre, neat HIPS and the untreated SPF-HIPS composites, respectively. The degradation level of sugar palm fibre was almost similar to that of other natural fibres. It was differentiated by the variability of three main natural fibre components, namely, hemicelluloses, cellulose and lignin, while sugar palm fibre was subjected to the heating decomposition of each component that takes place in three steps. The first one was initial weight loss at 56 to 165°C, known as moisture evaporation and the loss of volatile extractives. Kim *et al*. (2004) reported that the initial mass loss took place from 50 to 150°C for natural fibre from rice husk and wood fibre. Meanwhile, Ishak *et al*. (2011) found that the range for this step was 45 to 123°C and Zainudin *et al*. (2009) stated their findings at 35 to 115°C for banana pseudo-stem fibre. These differences occurred due to the diversity of water and volatile extractive content in the fibres. The TG analysis data showed that at 56°C, the initial mass loss was at 99.7% weight and at 165°C, the weight was 89%. These findings indicated that 10.7% moisture and volatile extractive content had been removed from the fibre.

The second step was the decomposition of hemicelluloses components at temperature ranging from 238 to 306°C, and the peak temperature for this phase was 287.4°C. This result was almost similar to that of Yang *et al*. (2007) who reported that the temperature ranging from 220 to 318°C and peak temperature was at 281°C for hemicelluloses component. The degradation of the cellulose component started from 306°C and ended at 387.4°C, with a peak temperature of 344.46°C. The lignin degradation was not clearly seen in this curve. Yang *et al*. (2007) reported in their work that lignin is tough and the degradation of lignin takes place from 165°C up to 900°C. It was difficult to show the peak temperature for lignin degradation because the maximum mass loss rate was less (i.e. about 0.1 %/min.). From this study, it is worth saying that lignin starts to decompose at about 238°C, whereas hemicelluloses starts to degrade at 238°C. The degradation of lignin gradually takes place during the heating process
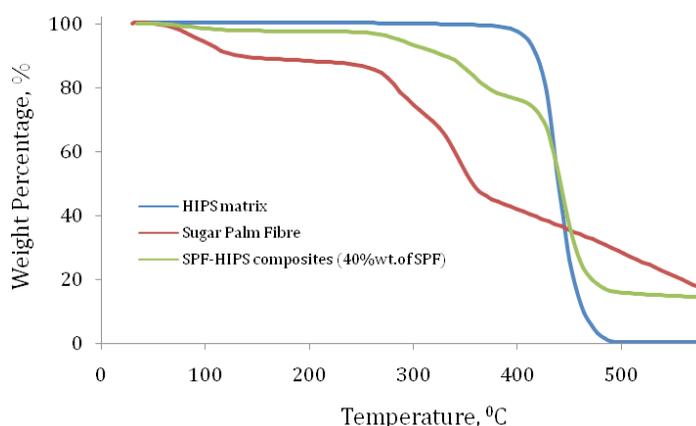

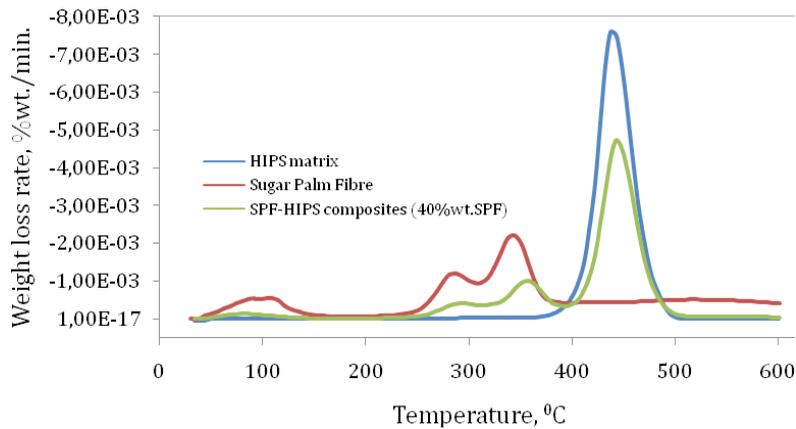Fig.1: TGA curve of sugar palm fibre, HIPS polymer matrix and SPF-HIPS composites.

Fig.2: Derivative TG curve of sugar palm fibre, HIPS polymer matrix, and SPF-HIPS composites.

until the end at 600°C. The degradation of lignin was unidentifiable as an individual peak in the DTG curve, and this was probably because it had overlapped with the hemicelluloses and cellulose decomposition (Reed & Williams, 2004).

Thermal decomposition of HIPS matrix takes place in one single stage between 365°C and 500°C, when the polymeric chains break down and evolve into the gaseous phase (see Fig.1 and Fig.2). Almost similar results were also exhibited by other researchers (see Siregar *et al*., 2011; Vilaplana *et al*., 2007; Agung *et al*., 2011). The peak of thermogram indicating the temperature of the maximum decomposition rate appears at around 437.86°C. Vilaplana *et al*. (2007) studied the degradation of several recycle HIPS polymer. The onset (initial) temperature of the thermal decomposition has similar values for all the HIPS materials at around 365°C. Meanwhile, the temperature of the maximum decomposition rate appears at around 430°C for all the samples (Vilaplana *et al*., 2007). A summary of all the decomposition stages for sugar palm fibre, HIPS matrix and the composites is shown in Table 1.

TABLE 1: Decomposition stages of sugar palm fibre, HIPS matrix and untreated SPF-HIPS composites.

Stage	Temperature	Sugar Palm Fibre, in °C	Neat HIPS, in °C	Untreated SPF-HIPS composites (40%wt.), in °C
1	Initial weight loss, T_i	56	-	42
	Final weight loss, T_f	165	-	146
	Temp. at max. degrad., T_m	109.3	-	79.5
2	Initial weight loss, T_i	238	-	266.8
	Final weight loss, T_f	306	-	321
	Temp. at max. degrad., T_m	287.4	-	291
3	Initial weight loss, T_i	306	-	329.97
	Final weight loss, T_f	387.4	-	387.5
	Temp. at max. degrad., T_m	344.46	-	356.25

TABLE 1: (continue)

4	Initial weight loss, T_i	-	365	405.4
	Final weight loss, T_f	-	500	510
	Temp. at max. degrad., T_m	-	437.86	439.74

The degradation temperatures for the natural fibre reinforced composites usually fall between the degradation temperatures for the matrix and the fibres (Singha & Thakur, 2008). The same behaviour is also exhibited by the untreated sugar palm fibre reinforced with high impact polystyrene composites. It has been observed that for composites that the initial decomposition temperature is at 42°C and the final decomposition of the composite at 600°C, indicating that the presence of cellulose fibres does affect the degradation process. The whole degradation of the untreated composites occurs in four stages. The first stage is the moisture evaporation which starts at 42°C and ends at 146°C, with the peak temperature at 79.6°C. In this step, it can be seen that the moisture content was less, as indicated by a tiny peak at DTG curve. The second stage of weight loss occurred at 266.8°C to 321°C, with the peak of this transition at 291°C. This step of degradation indicated the decomposition of hemicelluloses content in the composites. The third step indicated the degradation of cellulose that occurred from 329.97 to 387.5°C, with the temperature at the maximum degradation at 356.25°C. The fourth step indicated the degradation of the HIPS polymer part in the composites that occurred from 405.4 to 510°C and the peak of this transition was observed at 439.74°C. The value is slightly higher than the peak transition of neat HIPS matrix. Hence, it can be stated that the thermal stability of SPF-HIPS composites is better than the neat HIPS.

TGA/DTG for the Treated SPF-HIPS Composites

Fig.3 represents the TG analysis of the SPF-HIPS composites after the treatments, while Fig.4 depicts the DTG thermogram. The compatibilizing agent and alkali-treated SPF fibre on the composites slightly influence the characteristics of the thermal degradation of the composites.

For 2% MA-g-PS and 3% MA-g-PS composites, the degradation occurs in three stages, as also shown by the degradation of the untreated composites. The first stage is believed to be the decomposition of the hemicellulose component, with an initial decomposition temperature at 260°C and the final temperature at 320°C, while the peak of transition occurs at 291°C. The second stage is the decomposition of cellulose component ranging from 331°C to 417°C, and the peak was observed at about 359.38°C and 359.46°C for 2%MA-g-PS and 3%MA-g-PS composites, respectively. The last stage is the degradation of HIPS polymer in the composites that occurs initially at 416°C to 500°C, and the peak of transition temperature occurs at about 444°C. Meanwhile, at the peak temperature transition for the untreated composites (439°C), it was clearly seen that the TG curve of the compatibilizing agent modified composites was higher as compared to the untreated composites.

The compatibilizer was found to improve the thermal resistance of the composites due to the good interaction between the natural fibre and the polymer matrix that was caused by the formation of a covalent bond at the interface (Doan *et al.*, 2007).
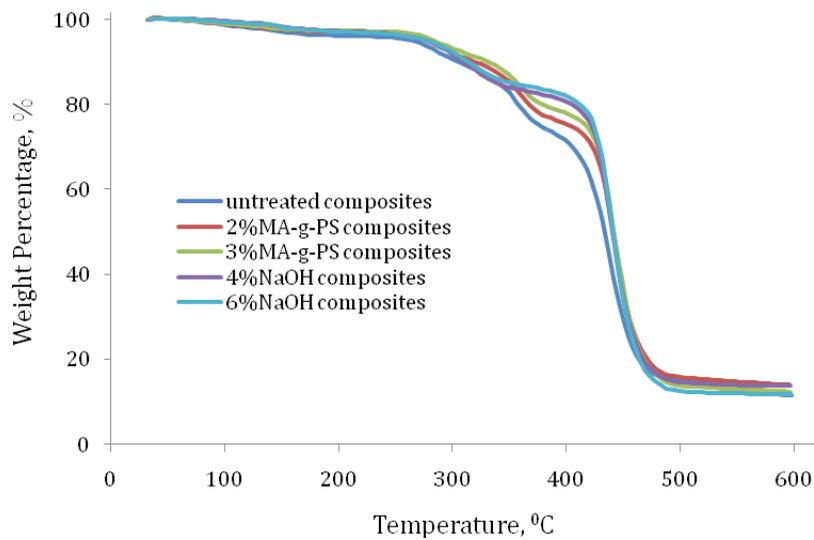
Fig.3: The TG analyses of the untreated and treated SPF-HIPS composites
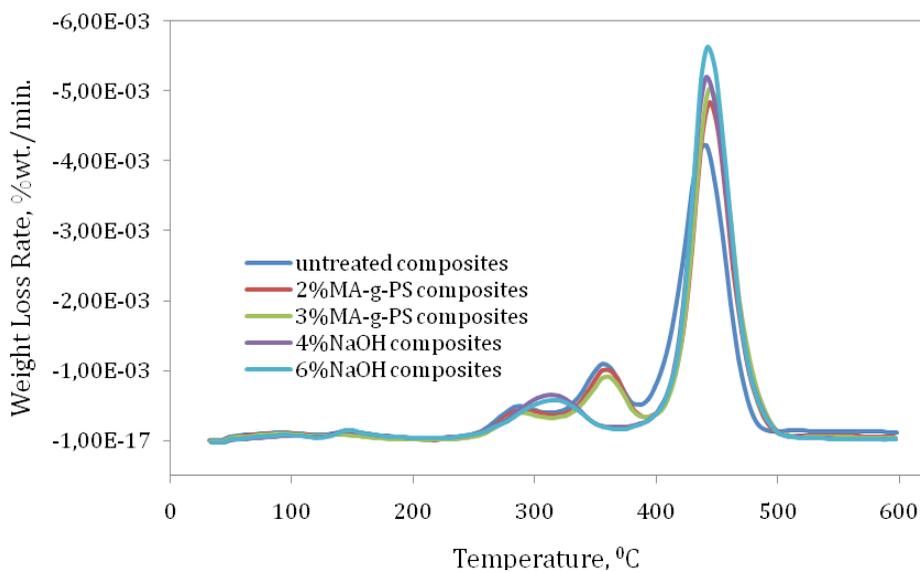

Fig.4: The DTG curve of the untreated and treated SPF-HIPS composites

The TG and DTG thermograms of the thermal decomposition treated fibre composites, with 4% and 6% of NaOH, showed different curves as compared to the TG and DTG curves of the untreated and compatibilizing agent treated composites. Only two stages appeared in the DTG curve during the degradation of the composites process. In general, this treatment removed natural and artificial impurities, produced a rough surface topography and made fibre fibrillation (Alawar *et al.*, 2009). Moreover, the alkali treatment changes the structure of the fibres, removes weak amorphous components (hemicellulose and lignin) so that the

fibre retains crystalline components (cellulose) (Reddy *et al*., 2012). It was believed that the structure change in the sugar palm interior due to the DTG curve exhibits the single step for degradation of hemicellulose and cellulose components. The initial degradation of this transition was at about 261°C to the final transition temperature at about 360°C, and the peak transition temperature occurred at about 311°C. It showed a lower value than the peak transition temperature of the untreated and Ma-g-PS treated composites for the degradation of cellulose component. Otherwise, the peak transition temperature in the next step is for the HIPS matrix component in the composites which shows an almost similar value to the Ma-g-PS treated composites which was about 442°C. However, all the peak transition temperatures of the treated composites at the degradation step of the HIPS component in the composites show a higher value than the untreated composites. It was worth noting that the thermal stability of the treated composites with alkali and compatibilizing agent was higher than that of the untreated composites. The degree of thermal stability was also exhibited by the residue that remained after the heating process. Table 2 represents the percentage weight of the sample at several temperature processes. Meanwhile, Table 3 represents the residue content of the samples at 600°C. On each temperature, it can be seen that the percentage weight of the treated samples has higher values than those of the untreated composites.

TABLE 2: Weight percentage of the samples at various temperatures

Samples	200 °C (%wt.)	300 °C (%wt.)	400 °C (%wt.)	500 °C (%wt.)
Untreated composites	96.2	90.5	71.6	15.3
2%MA-g-PS composites	97.09	92.2	75.1	15.8
3%MA-g-PS composites	97.37	93.2	78	13.8
4%NaOH composites	97.26	92	80.5	14.6
6%NaOH composites	97.15	92.4	81.9	12.52

TABLE 3: Residue of the samples as the TG analysis results

Samples	Residue at 600°C (% wt.)
Sugar Palm Fibre	14.4
Neat HIPS matrix	0.39
Untreated composites (40%wt.SPF)	11.27
2% MA-g-PS composites	13.89
3% MA-g-PS composites	12.48
4% NaOH composites	13.73
6% NaOH composites	11.82

CONCLUSION

The effects of alkaline treatment and compatibilizing agent on the thermal degradation of sugar palm fibre reinforced high impact polystyrene composites were studied in the current work. The modification of the SPF-HIPS composites, using the compatibilizing agent with different weight concentrations of polystyrene-block-poly(ethylene-ran-butylene)-blockpoly(styrene-graft-maleic anhydride) and the fibres treated with alkali, has brought a slight improvement to the peak temperature of decomposition of composites. It can be stated that the addition of sugar palm fibre and the modification of the composites with alkaline treatment and compatibilizing agent on the high impact polystyrene composites resulted in a higher thermal stability of the composites than the high impact polystyrene polymer alone.

ACKNOWLEDGEMENTS

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