

Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetric (DSC) Analysis of Pineapple Leaf Fibre (PALF) Reinforced High Impact Polystyrene (HIPS) Composites

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ABSTRACT

This paper studied the thermal behaviour of pineapple leaf fibre (PALF) reinforced high impact polystyrene (HIPS) composite. Thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) analysis were used to measure the thermal characteristic of HIPS/PALF composites. In particular, the TGA analysis was utilized to measure the degradation and decomposition of materials in neat polystyrene, pineapple fibre, and the composites. The measurements were carried out in the temperature of 25°C – 800°C, at a heating rate of 20°C min⁻¹ and the nitrogen gas flow was 50 mL min⁻¹. The temperature of the DSC analysis was programmed to be between 25°C – 300°C. The results from TGA analysis show that the addition of pineapple fibre has improved the thermal stability of the composites as compared to neat HIPS. In addition, the effects of compatibilising agent and surface modification of PALF with alkali treated were also determined and compared.

Keywords: Pineapple leaf fibre, natural fibre composites, high impact polystyrene (HIPS), TGA, DSC

INTRODUCTION

Thermal analysis is a very useful and important method to be used to characterize any materials, including thermoplastic or thermosetting polymer matrix, as well as to determine the influence of natural fibres addition into the polymers (George *et al.*, 1996; Luz *et al.*, 2008). One of the accepted methods for studying the thermal properties of polymeric materials is the thermogravimetric analysis (TGA). TGA is a thermal analysis technique that has been used to measure changes in the weight loss (mass) of sample that is subjected to a steady increase of temperature so as to quantify reactions involving gaseous emissions (Villain *et al.*, 2007; Reis *et al.*, 2007). Meanwhile, the differential scanning calorimetric analysis (DSC) was used to measure a melting point and phase transition of the composites.

The degradation of natural fibre with TGA analysis has been investigated in some previous studies. The decomposition natural fibres occurs in two or three stages of loss weight processes under controlled temperature between 25°C to 800°C (Araujo *et al.*, 2008; Brigida *et al.*, 2010; Arbelaitz *et al.*, 2006). It is important to note that the different loss weight processes are dependent upon

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the types and sources of natural fibres. Meanwhile, the degradation of polymeric matrix materials, particularly the HIPS, has taken place in a single stage between 350°C and 500°C (Vilaplana *et al.*, 2007). The temperature of the maximum decomposition of HIPS is around 430°C and the weight of residue is about 1.2%.

In the DSC analysis, glass transition temperature (T_g) is related to the mobility of the polymeric chains and it determines the transition between the glassy and the rubbery polymeric state (Vilaplana *et al.*, 2007). The investigation of glass transition PS/sisal composites with dynamic mechanical analysis was carried out by Nair *et al.* (2001) who found that the glass transition temperature (T_g) of neat polystyrene was higher compared to the composites that contained a sisal fibre. The glass transition temperature of neat polystyrene was found to be 107.55°C, while the composites with 10, 20, and 30 wt% sisal fibre were at 89.71°C, 94.28°C, and 100.05°C, respectively. The objective of this study was to observe the thermal properties of the HIPS/PALF composites under the TGA and DSC analysis.

MATERIALS AND METHODS

Materials

The high impact polystyrene (HIPS) that has been used as the polymer matrix is Idemitsu PS HT 50, which was supplied by Petrochemical (M) Sdn. Bhd., Pasir Gudang, Johor, Malaysia. The pineapple leaf fibre (PALF) was obtained from Pemalang, Central of Java, Indonesia. The size of the pineapple leaf fibre used in this study was 10-40 mesh. There are two types of compatibilising agent used in this research, namely polystyrene-block-poly(ethylene-ran-butylene)-block-poly(styrene-graft-maleic anhydride), and poly(styrene-co-maleic anhydride). Sodium hydroxide (NaOH) that was also used to treat the pineapple leaf fibres was supplied by Aldrich Chemical Company, Malaysia.

Compatibilising Agent

Three different weight concentrations (2, 4, and 6 wt%) of compatibilising agent were applied for both types of compatibiliser. The weight of the short PALF (i.e. 50 wt% of the total formulation) was kept constant while the ratio of HIPS and compatibilising agent were also varied, as given in Table 1 below.

TABLE 1
Denotation of sample

Sample	Materials			
	HIPS [%]	PALF [%]	Compatibilising agent [%]	
			Polystyrene-block-poly (ethylene-ran-butylene)-block-poly (styrene-graft-maleic anhydride)	Poly (styrene-co-maleic anhydride)
HIPS 100	100	0	0	0
HIPS/PALF	50	50	0	0
CFA2	48	50	2	0
CFA4	46	50	4	0
CFA6	44	50	6	0
CFB2	48	50	0	2
CFB4	46	50	0	4
CFB6	44	50	0	6

Alkali (NaOH) Treatment

The PALF was soaked in two different concentrations (2% and 4%) of NaOH solution in a water bath for 1 hour at room temperature. The ratio of the fibres to the solution was 1:20 (w/v). After the treatment, the fibres were washed, rinsed several times with distilled water, and then dried in an oven at 80°C for 24 hours. The fibre treated with 2% NaOH and denoted with TFA2 for 4% is TFA4.

Composite Processing

The PALF fibres were incorporated into the HIPS matrix using a Brabender Plasticorder intensive mixer, model PL2000-6 at 165°C. The mixing process was performed in the following order. First, the HIPS and compatibilising agent were placed inside the mixing chamber for about 2 minutes at 50 rpm; later, the PALF was added into the mixing chamber for 10 minutes. The total mixing process took about 12 minutes.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was carried out using a Mettler Toledo SDTA 851 analyzer. The samples weighing between 7-20 mg were placed in ceramic crucibles, while the tests were carried out in nitrogen atmosphere. The heating rate of the samples was 20°C min⁻¹.

Differential Scanning Calorimetric (DSC)

The preparation of the samples that were used for the differential calorimetric was similar to the TGA. Meanwhile, the analysis in the DSC was performed using the Mettler Toledo DSC822 analyzer. The temperature was programmed in the range of 25°C to 300°C, under nitrogen atmosphere.

RESULTS AND DISCUSSIONS

Thermogravimetric Analysis (TGA)

In this study, the Thermogravimetric (TGA) curves were used to determine the thermal degradation and thermal stability of each material. The TG analysis of neat high impact polystyrene (HIPS), pineapple leaf fibre (PALF) and their composites are presented in *Fig. 1*. The thermal decomposition of each sample took place in a programmed temperature range of 25°C to 800°C. The neat HIPS showed only one stage of weight loss process, which had a transition temperature that began from 341°C and the final transition at 483°C, and it was clear that the peak transition temperature of HIPS at 418°C. The weight loss and residual weight of HIPS for the TG analysis were found to be 98% and 2.4%, respectively (*see* Table 2). Previous studies (Vilaplana *et al.*, 2007) have observed thermogravimetric of virgin HIPS using the same instrument analyzer. They found that the thermal decomposition of HIPS occurred in one single stage, i.e. between 369°C – 490°C and temperature maximum transition at 433°C. The percentage of the residual weight of HIPS gathered in their study was 1.2%. The other investigation (Nair *et al.*, 2001) of the thermogravimetric neat polystyrene showed that the decomposition of PS started at 288°C and there are four stages of weight loss process.

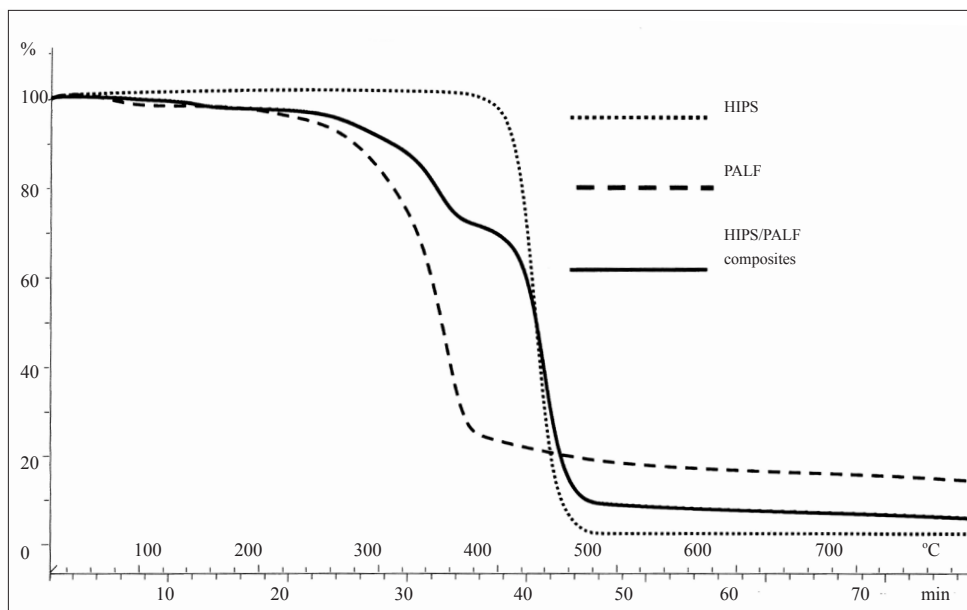


Fig. 1: The TG analysis of HIPS, PALF and HIPS/PALF composites

The thermal decomposition of PALF under nitrogen atmosphere comprises of a two-step process. The first step process that was shown at temperature 25°C to 103°C had a weight loss of 2.4%. Several previous studies (e.g. Threepopnatkul *et al.*, 2009; De Rosa *et al.*, 2010) revealed that the loss weight of this stage was due to the release of absorbed moisture or vaporization of the water from the fibres. George *et al.* (1996) reported that the weight loss of pineapple fibre at 100°C was about 6%, while at 200°C and 300°C, the weight loss were about 7.6% and 16%, respectively. The second stage of weight loss occurred at 126°C - 542°C, with the peak of this transition at 339°C. This weight loss indicated the decomposition of cellulose (George *et al.*, 1996). In their study, the thermal decomposition of pineapple fibre was obtained at 350°C. Meanwhile, the thermal decomposition for other natural fibres, such as sisal and flax fibres, occurred at 340°C and 345°C, respectively (Manfredi *et al.*, 2006). Compared to these natural fibres, the thermal decomposition of pineapple fibre in this study was slightly lower than the thermal stability. Meanwhile, the residual weight of PALF in the temperature that ranged between 25°C - 800°C was 17% (*see* Table 2). Devallencourt *et al.* (1996) reported that the residual weight of cellulose, after heating from 20 to 900°C, was about 17% and they explained that the results for the final products from the degradation of cellulose under an inert atmosphere were carbonaceous residues plus undegraded fibres when they did not remain after heating.

As illustrated in Table 2, the degradation steps are in the temperature range of 72°C - 182°C, 202°C - 367°C, and 371°C - 479°C, while the maximum peak of the transition temperature for these steps were 139°C, 338°C, and 425°C. The percentage of the loss weight composites at corresponding transition was 2.6, 26, and 62%, respectively. Therefore, it can be concluded that the thermal stability of the composites had a higher value as compared to neat HIPS.

TABLE 2
Results of the TG analysis HIPS, PALF and its composites

Sample	No. of transition	Transition temperature (°C)			Weight loss at transition (%)	Residual weight (%) at 800°C
		T _i	T _m	T _r		
HIPS	1	341	418	483	98	2.4
PALF	1	36	69	104	2.4	17
	2	126	339	542	81	
HIPS/PALF composites	1	72	139	182	2.6	9
	2	202	338	367	26	
	3	371	425	479	62	

The Effects of Compatibilizing Agent and Alkali Treated Fibre on the TG Analysis

Fig. 2 presents the effects of compatibilising agent and alkali-treated PALF fibre on the thermal degradation of the composites. All the sample materials exhibited a three-stage degradation process. Meanwhile, the composites using compatibilizer of *polystyrene-block-poly(ethylene-ran-butylene)-block-poly(styrene-graft-maleic anhydride)* showed the maximum peak temperature decomposition of composites at 428°C. It was clear that the TG curve of the modified HIPS/PALF composites was higher compared to the untreated ones. The modification of the natural fibre reinforced polymer composite using modifier or compatibilizer was found to improve the thermal resistance of the composites due to the stronger interaction between the natural fibre and the polymer matrix that was caused by the formation of the covalent bond at the interface (Doan *et al.*, 2007). Meanwhile, the increase compatibilizer of *poly(styrene-co-maleic anhydride)* from 2-6 wt.% decreased the thermal stability of the composites. The thermal decomposition treated fibre composites, with 2% and 4% of NaOH, was found at the temperature 428°C. This result is similar to the modification of fibres using compatibilizer (CFA2, CFA4, and CFA6). Meanwhile, the fibres treated with caustic soda enhanced the thermal stability of natural fibre. This treatment removed natural and artificial impurities, produced a rough surface topography and made fibre fibrillation (Alawar *et al.*, 2009).

Table 3 shows the weight loss of all composites at the first stage transition temperature (<200°C)

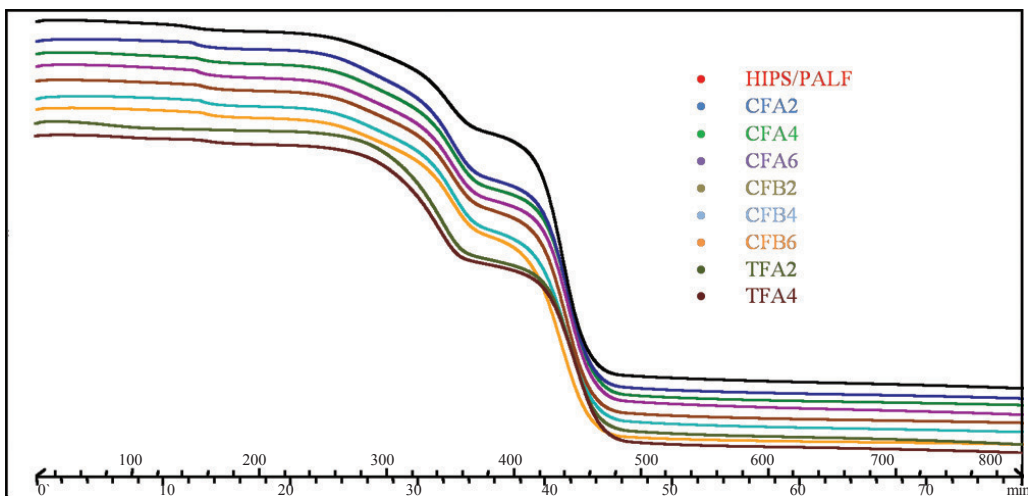


Fig. 2: The TG curves showing the effects of the compatibilising agent and alkali-treated fibre

in the range of 1.1% to 1.9%. At the second stage (<400°C), the weight loss of the composites was around 31%-36% and at the third stage of transition temperature (<600°C), the weight loss ranged from 48%-53%. The total residual weight of all the composites at 800°C was in the range of 12%-15%.

TABLE 3
The TG analysis of the effects of compatibilising agent and alkali-treated fibre

Sample	No. of transition	Transition temperature (°C)			Weight loss at transition (%)	Residual weight (%) at 800°C
		T _i	T _m	T _r		
CFA2	1	121	145	176	1.8	14.8
	2	204	339	372	32	
	3	373	428	483	51	
CFA4	1	125	149	178	1.7	12.1
	2	202	339	374	32	
	3	374	428	490	53	
CFA6	1	118	147	176	1.7	12.2
	2	204	338	375	32	
	3	374	428	483	52	
CFB2	1	128	150	182	1.8	13.1
	2	203	338	367	31	
	3	373	425	481	53	
CFB4	1	119	148	172	1.9	14.6
	2	200	338	367	32	
	3	370	423	480	50	
CFB6	1	132	150	177	1.6	12.6
	2	197	339	368	31	
	3	369	422	478	53	
TFA2	1	129	148	170	1.2	12.7
	2	220	327	361.	36	
	3	372	427	490.	48	
TFA4	1	134	151	172	1.1	12.8
	2	208	325	357	33	
	3	369	428	485	50	

Differential Scanning Calometric (DSC)

The DSC curve of the HIPS, PALF, and HIPS/PALF composites are shown in *Fig. 3*, while the values of these materials are summarized in Table 4. The glass transition (T_g) of HIPS at 105°C, while the melting point (T_m) at the temperature 150°C. The findings of other studies showed that the glass transition and melting point of HIPS were at 90°C and 120°C or 160°C, respectively (Vilaplana *et al.*, 2007). The glass transition (T_g) of PALF from this study occurred at 75°C. Meanwhile, the addition of PALF to reinforce HIPS increased the T_g value of the composites. It could be seen that the temperature of T_g HIPS/PALF composite was at 123°C, indicating that the temperature T_g of the composite increased around 18°C as compared to neat HIPS.

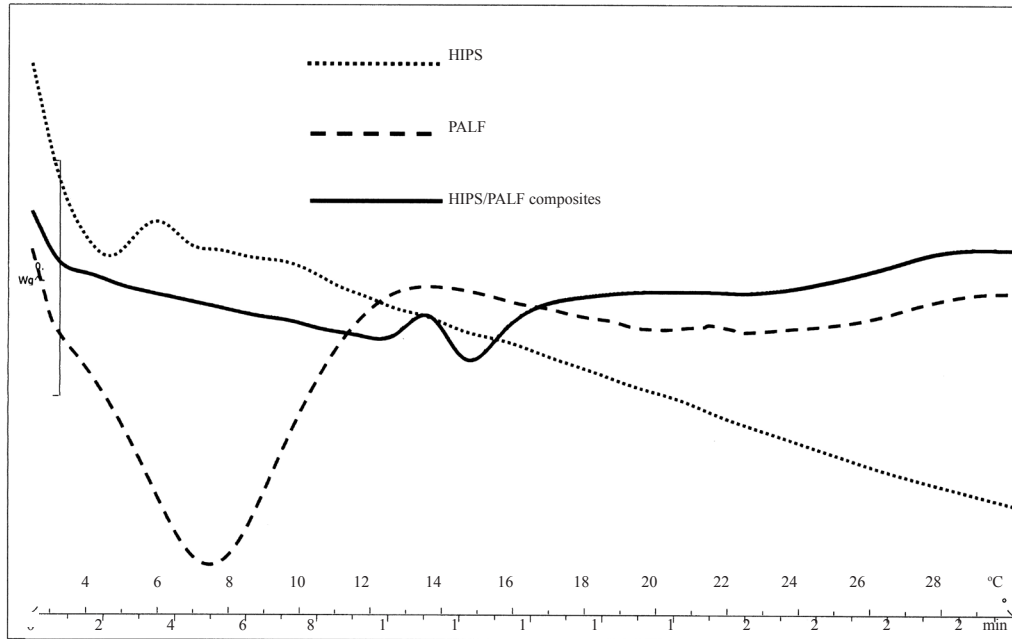


Fig. 3: The DSC analysis of HIPS, PALF and HIPS/PALF composites

The Effects of Compatibilizing Agent and Alkali-treated Fibres on the DSC Analysis

Fig. 4 presents the DSC curve of the composites using compatibilising agents. The addition of compatibilizer into the composites, with different weight concentrations of *polystyrene-block-poly(ethylene-ran-butylene)-block-poly(styrene-graft-maleic anhydride)*, decreased the glass transition and melting point of the composites. As shown in Table 4, the glass transition of the composites, denoted with CFA2, CFA4 and CFA6, was about 118°C, 104°C, and 102°C. The melting point also decreased at 149°C, 147°C, and 147°C, respectively. The increase of *poly(styrene-co-maleic anhydride)* that modified the HIPS/PALF composites (CFB2, CFB4, and CFB6) also decreased the glass transition of the composites, but the melting temperature of the composites was found to be similar to the untreated fibre composites.

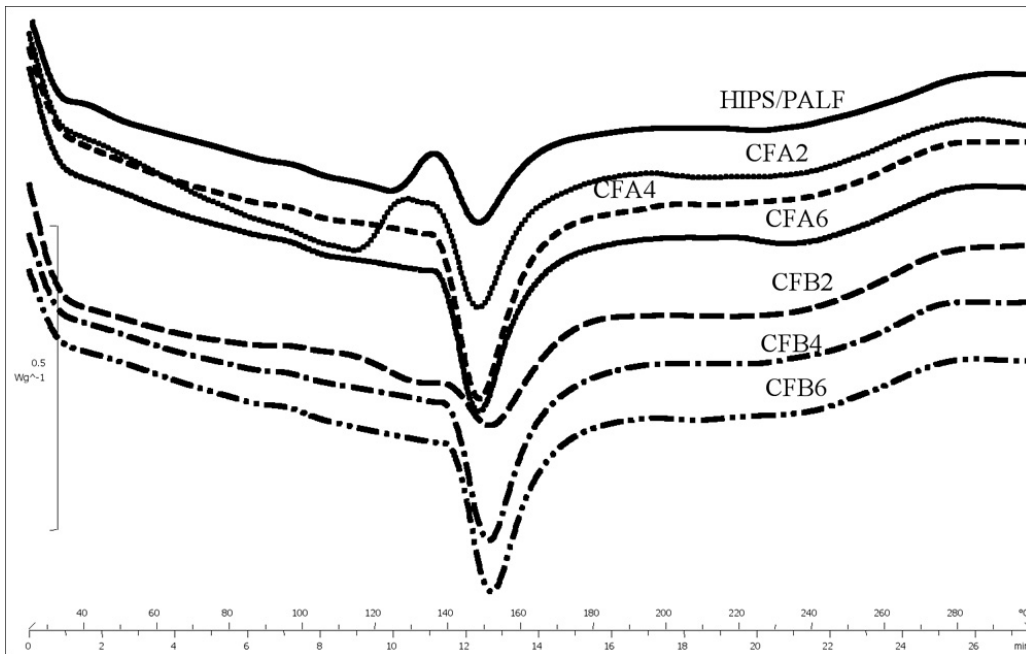


Fig. 4: The DSC curves of the composites using compatibilizer

TABLE 4
The DSC analysis of the HIPS/PALF composites

Sample	T_g , glass transition °C	T_m , melting point (°C)
HIPS	105	150
PALF	75	-
HIPS/PALF	123	149
CFA2	118	149
CFA4	104	147
CFA6	102	147
CFB2	99	150
CFB4	96	150
CFB6	95	151
TFA2	106	152
TFA4	105	151

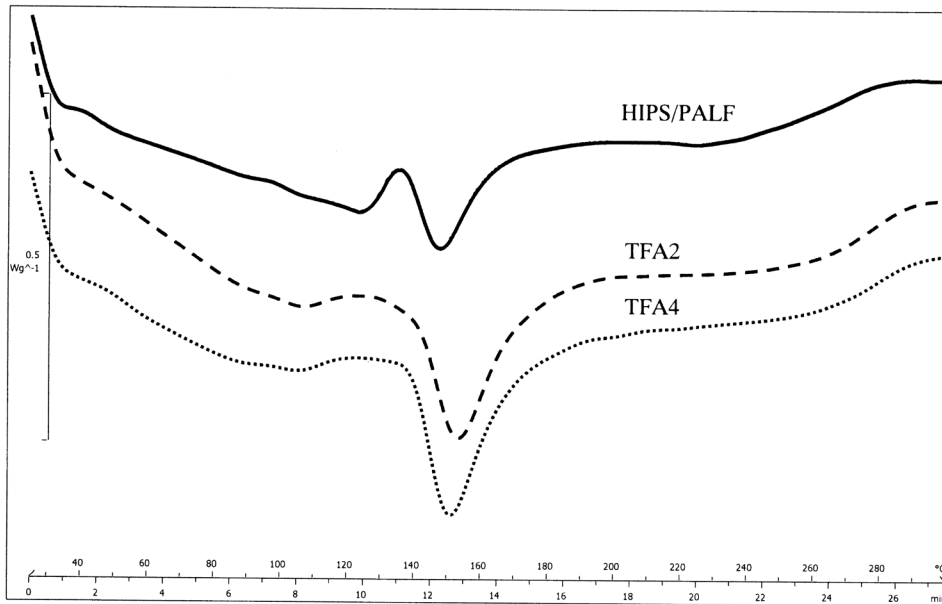


Fig. 5: The DSC curves of the alkali-treated fibre composites

Fig. 5 presents the DSC curves of the untreated and treated fibre composites. The glass transition (T_g) temperature of alkali-treated fibre composite, with 2% (TFA2) and 4% (TFA4) of NaOH, was shown at 106°C and 105°C. The melting temperature of these composites was 152°C and 151°C, respectively. This value is similar to the glass transition of neat HIPS and only small improvement was observed at the melting temperature of the composites. As compared to the untreated fibre composite, the glass transition of the treated fibre composite was shown to be lower, but the melting temperature was higher.

CONCLUSIONS

Based on the results of this study, it can be concluded that the addition of PALF for the reinforced HIPS composites has increased the thermal decomposition and glass temperature (T_g) of the composites. The modification of the HIPS/PALF composites, using the compatibilising agent with different weight concentrations of *polystyrene-block-poly(ethylene-ran-butylene)-block-poly(styrene-graft-maleic anhydride)* and the fibres treated with alkali, has brought a slight improvement to the thermal decomposition of composites. Meanwhile, the modification composites using *poly(styrene-co-maleic anhydride)* decreased the thermal decomposition as compared to the untreated fibre. However, no significant improvement was found on the melting temperature of composites with the addition of compatibilizer and the fibre that was treated with alkali solution.

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REFERENCES

- Alawar, A., Hamed, A. M. and Al-Kaabi, K. (2009). Characterization of treated palm tree fibre as composites reinforcement. *Composites: Part B*, 40, 601-606.
- Araujo, J.R., Waldman, W.R. and De Paoli, M.A. (2008). Thermal properties of high density polyethylene composites with natural fibres: Coupling agent effect. *Polymer Degradation and Stability*, 93, 1170-1175.
- Arbelaz, A., Fernandez, B., Ramos, J.A. and Mondragon, I. (2006). Thermal and crystallization of short flax fibre reinforced polypropylene matrix composites: Effect of treatment, *Thermochimica Acta*, 440, 11-121.
- Brigida, A.I.S., Calado, V.M.A., Goncalves, L.R.B. and Coelho, M.A.Z. (2010). Effect of chemical treatments on properties of green coconut fibre. *Carbohydrate Polymers*, 79, 832-838.
- De Rosa, I.M., Kenny, J.M., Puglia, D., Santulli, C. and Sarasini, F. (2010). Morphological, thermal and mechanical characterization of okra (*Abelmoschus esculentus*) fibres as potential reinforcement in polymer composites. *Composites Science and Technology*, 70, 116-122.
- Devallencourt, C., Saiter, J.M. and Capitaine, D. (1996). Characterization of recycled cellulose: Thermogravimetry/Fourier transform infra-red coupling and thermogravimetry investigations. *Polymer Degradation and Stability*, 52, 327-334.
- Doan, T.T.L., Brodowsky, H. and Mader, E. (2007). Jute fibre/polypropylene composites II. Thermal hydrothermal and dynamic mechanical behaviour. *Composites Science and Technology*, 67, 2707-2714.
- George, J., Bhagawan, S.S. and Thomas, S. (1996). Thermogravimetric and dynamic mechanical thermal analysis of pineapple fibre reinforced polyethylene composites. *Thermal Analysis*, 47, 1121-1140.
- Luz, S.M., Del Tio, J., Rocha, G.J.M., Goncalves, A.R. and Del' Arco Jr., A.P. (2008). Cellulose and cellulignin from sugarcane bagasse reinforced polypropylene composites: Effect of acetylation on mechanical and thermal properties. *Composites Part A: Applied Science and Manufacturing*, 39, 1362-1369.
- Manfredi, L.B., Rodriguez, E.S., Przybylak, M.W. and Vasquez, A. (2006). Thermal degradation and fire resistance of unsaturated polyester, modified acrylic resins and their composites with natural fibres. *Polymer Degradation and Stability*, 91, 255-261.
- Nair, K.C.M., Thomas, S. and Groeninckx, G. (2001). Thermal and dynamic mechanical analysis of polystyrene composites reinforced with short sisal fibres. *Composites Science and Technology*, 61, 2519-2529.
- Reis, P.N.B., Ferreira, J.A.M., Antunes, F.V. and Costa, J.D.M. (2007). Flexural behaviour of hybrid laminated composites. *Composites Part A: Applied Science and Manufacturing*, 38, 1612-1620.
- Threepopnatkul, P., Kaerkittha, M. and Anthipongarporn. (2009). Effect of surface treatment on performance of pineapple leaf fibre-polycarbonate composites. *Composites: Part B*, 40, 628-632.
- Vilaplana, F., Ribes-Greus, A. and Karlsson, S. (2007). Analytical strategies for the quality assessment of recycled high impact polystyrene: A combination of thermal analysis, vibrational spectroscopy, and chromatography. *Analytica Chimica Acta*, 604, 18-28.
- Villain, G., Thiery, M. and Platret, G. (2007). Measurement methods of carbonation profiles in concrete: Thermogravimetry, chemical analysis and gammadensimetry. *Cement and Concrete Research*, 37, 1182-1192.