

# The Thermal Properties of Low Density Polyethylene (LDPE)/Palm Kernel Shells (PKS) Composites: Effect of coupling agent

B. Y. Lim<sup>1</sup>, H. Salmah and P. L. Teh  
School of Materials Engineering, Universiti Malaysia Perlis,  
Taman Muhibah, 02600 Jejawi, Perlis  
Email: <sup>1</sup>bying425@yahoo.com

## Abstract

*The thermal properties of Low Density Polyethylene (LDPE)/Palm Kernel Shell (PKS) composites were studied. The comparison of thermal properties of LDPE/PKS composites with coupling agent, coconut oil coupling agent (COCA) and chemical modification with acrylic acid (AA) were investigated. The thermal degradations of LDPE/PKS composites were the combined phenomenon of the degradation of LDPE and PKS. The presence of the filler in LDPE polymeric matrix improved the thermal stability of the composites. The thermal stability of LDPE/PKS composites with COCA is better than LDPE/PKS with AA.*

## 1. Introduction

For the past two decades, natural fillers have been used in the polymeric composites as fillers. Natural fillers possess many advantages such as biodegradable, renewable, inexpensive and readily available from natural resources. Besides, they are non-abrasive and hence able to reduce the machine wear during processing. The energy consumption for natural filler during processing is lower compare to synthetic filler such as glass fiber. Several studies have been conducted to generate natural filler filled polymeric composites [1-9].

Though the natural fillers possess many advantages, there are some drawbacks in the due to the different nature of the filler and polymers. Incompatibility between fibers and polymer matrices, the tendency to form aggregates during processing and the poor resistance to the moisture, reduce the use of natural fillers as reinforcement in polymers [10]. Incompatibility of components is responsible for the poor thermal and mechanical properties of the composites. Since natural fillers are hydrophilic while polymers are hydrophobic in nature, a coupling agent

is needed to promote better interfacial adhesion between the fillers and matrices.

It is important to understand the thermal properties of the organic filler filled polymeric composites in processing. The processing temperature of the organic filler is limited due to the potential filler degradation at higher temperature. Thus it is vital to determine the degradation temperature of the composites in order to produce good quality composites. However, it has been reported that the deterioration of properties is observed when processing temperatures are maintained below 200 °C [11].

In this study, the thermal properties of the LDPE, PKS/LDPE/PKS composites with coupling agents at different filler loading were determined using thermogravimetric analysis (TGA).

## 2. Experimental

### 2.1. Materials

The LDPE was supplied by Titan Chemical, Johor, Malaysia with density of 0.922 g/cm<sup>3</sup> and MFI of 0.33g/10min. The palm kernel shell that used as fillers was obtained from Malpom Oil Palm Processing, Nibong Tebal, Malaysia. The palm kernel shell was dried at 80 °C for 24 hours to evaporate the moisture content. Then the cleaned palm kernel shell was crushed into powder form. The average particles size of 75 μm was measured by Malvern particle size analyzer. The acrylic acid with molecular weight (Mw = 72.06), with density of 1.051 g/ml was supplied by Fluka. The ethanol was used as solvent to dissolve acrylic acid in filler treatment. The ethanol 96% was supplied by Fisher Scientific (M) Sdn. Bhd., Shah Alam. Coconut oil coupling agent (COCA) was synthesized by using ethylene diamine and lauric acid from virgin coconut oil.

## 2.2. Filler treatment

The acrylic acid (AA) delivered is in liquid form. PKS was mixed into 3% (v/v) of acrylic acid in ethanol. Then the solution was added into the flask with constant stirring for 1 hour. The treated filler was dried at 80 °C for 24 hours to evaporate completely the ethanol.

## 2.3. Composites preparation

Composites were prepared by using a Z-Blade mixer at temperature of 180 °C and rotor speed of 50 rpm. The LDPE were loaded into the mixing chamber for 5 minutes. After 5 minutes, filler was added and mixing continued for 10 minutes. The total mixing time of composites was 15 minutes. Finally, the composites were removed from the mixing chamber and pressed into thin sheet form in compression moulding. Compression moulding involved preheating at 180 °C for 9 minutes followed by compressing for 6 minutes and subsequent cooling under pressure for 4 minutes

The formulation of the LDPE/PKS composites is shown in Table 1.

Table 1. Formulations for LDPE/PKS composites

Materials	Composites	Composites + COCA	Composite + AA
LDPE (php)	100	100	100
PKS (php)	0, 20, 40	20, 40	0, 40
COCA (php)	-	3	-
AA (%)	-	-	5

## 2.4. Thermogravimetric analysis (TGA)

Thermogravimetric analysis was carried out using a Perkin Elmer Pyris Diamond TG/DTG. The samples, weighting about 15-25 mg, were subjected to heating rate of 20 °C/min at temperature range of 30 °C to 650 °C under nitrogen flow of 50 ml/min.

## 3. Results and discussions

Figures 1 and 2 show the thermogravimetric curves and derivative thermogravimetry curves of LDPE and PKS. There is only one weight loss process in LDPE, while two weight loss processes are found in PKS. It can be seen that the weight loss of PKS started at 40 °C. This is due to the evaporation of volatile and moisture content of PKS. The degradation started to take place more rapidly at 204 °C and finished at 379.2 °C. The derivative thermogravimetry (DTG) thermograph in Figure 2 shows two decomposition peaks for the PKS indicated its two-step degradation.

The first and second peaks temperature was 282 and 345 °C, respectively which showed the degradation of cellulose and lignin. According to Nicholas [12], cellulose decomposed at 280 °C and ended at 300 to 350 °C while lignin decomposed at 300 to 350 °C and ended at 400 to 450 °C. The weight loss of LDPE occurred in a one step degradation process from 400 to 500 °C. The LDPE started to weight loss at 280.9 °C and continued very slowly before reaching the temperature of 400 °C. Above 400 °C, the degradation process took place rapidly due to the further breakdown of the LDPE into gaseous products at higher temperature.

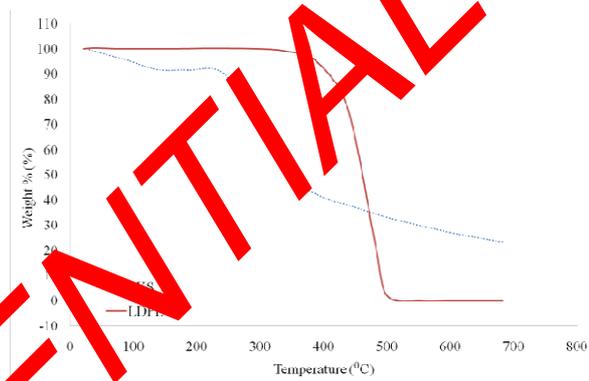


Figure 1. Thermogravimetric curves of LDPE and PKS

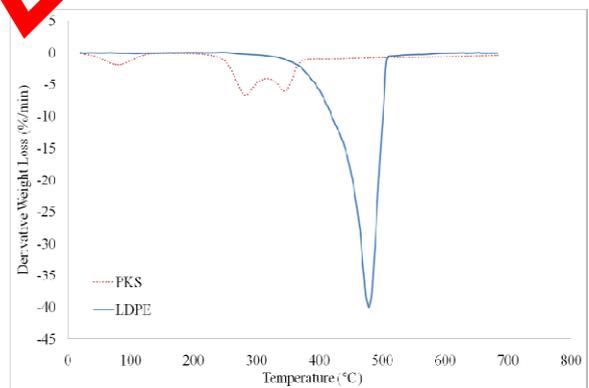


Figure 2. Derivative thermogravimetry (DTG) curves of LDPE and PKS.

From Figure 3, it can be seen that the onset temperature of the LDPE/PKS composites was lower compared to the LDPE. This may attributed to the lower onset temperature of the PKS. The thermal degradation of the LDPE/PKS composites was a combined phenomenon of thermal degradation of PKS and LDPE. Figure 3 shows that LDPE/PKS composites exhibited three steps degradation in the thermal

analysis. The first two steps degradation of weight loss at 290 to 370 °C were due to the degradation of PKS, while the following weight loss was caused by the degradation of LDPE at 470 to 500 °C.

Figure 3 shows the effect of COCA and AA on the thermogravimetric analysis of the LDPE/PKS composites at filler loading of 40 php. The derivative thermogravimetric (DTG) curves compared of composites different coupling agents were shown in Figure 4. The addition of the coupling agent had enhanced the thermal stability of the composites. Better interfacial bonding was established between the hydrophilic filler and the hydrophobic polymeric matrix.

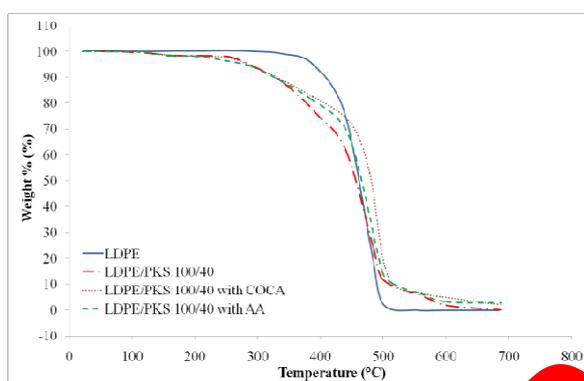


Figure 3. Comparison of thermogravimetric analysis of PKS, LDPE, and LDPE/PKS composites with different coupling agents.

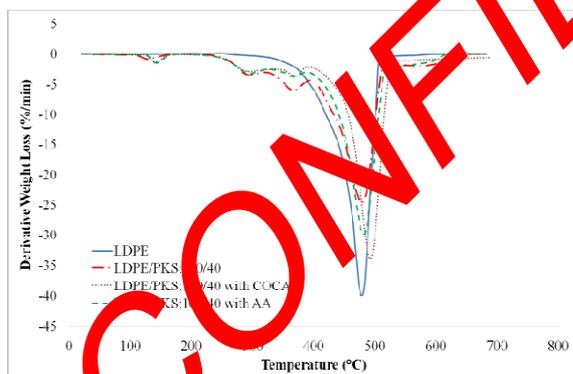


Figure 4. Comparison of derivative thermogravimetry (DTG) curves of PKS, LDPE, and LDPE/PKS composites with different coupling agents.

Table 2 summarized the derivative data (DTG) for the PKS, LDPE and LDPE/PKS composites with different coupling agent. At similar filler loading, the peak temperature of LDPE/PKS composites with

COCA was higher than LDPE/PKS composites with AA, followed by LDPE/PKS composites.

Table 3 shows the total percentage weight loss of PKS, LDPE and LDPE/PKS composites. PKS showed almost 73% weight loss and left 27% of residues. LDPE was 100% burnt in the thermal analysis. At higher PKS loading, LDPE/PKS composites have lower total weight loss. The addition of PKS improved the thermal stability of the composites. The addition of coupling agent was found to decrease the total weight loss. The total weight loss of LDPE/PKS composites is lowest compared to LDPE/PKS composite with AA followed by LDPE/PKS composites. The better thermal stability of composites with coupling agent was attributed to the better interfacial bonding between the LDPE polymeric matrix and the PKS with addition of coupling agent.

Table 2 Thermogravimetric analysis of PKS, LDPE, and LDPE/PKS composites with different coupling agents.

Sample	Onset Temperature (°C)	Peak Temperature (°C)			Offset Temperature (°C)
		1 <sup>st</sup> peak	2 <sup>nd</sup> peak	3 <sup>rd</sup> peak	
PKS	204.3	282.3	344.8	-	379.2
LDPE	280.9	478.0	-	-	508.8
LDPE/PKS : 100/20	250.4	291.7	369.5	487.7	659.5
LDPE/PKS : 100/40	237.4	290.0	364.0	474.4	635.2
LDPE/PKS : 100/20 with COCA	237.1	297.8	369.0	495.5	534.0
LDPE/PKS : 100/40 with COCA	225.3	293.4	368.2	493.9	530.3
LDPE/PKS : 100/20 with AA	236.0	295.4	365.4	485.3	612.8
LDPE/PKS : 100/40 with AA	218.8	292.6	364.6	478.0	610.9

Table 3 Percentage weight loss of PKS, LDPE, and LDPE/PKS composites with different coupling agents.

Temperature (°C)	Weight Loss (%)							
	PKS	Neat LDPE	LDPE/PKS : 100/20	LDPE/PKS : 100/40	LDPE/PKS : 100/20 with COCA	LDPE/PKS : 100/40 with COCA	LDPE/PKS : 100/20 with AA	LDPE/PKS : 100/40 with AA
100	6.77	0.05	0.18	0.35	0.10	0.14	0.14	0.20
200	1.69	0.04	0.82	1.29	1.03	1.57	0.93	1.66
300	21.54	0.12	2.89	4.84	3.00	4.80	3.24	5.16
400	28.87	7.20	8.69	18.52	8.37	11.94	10.33	13.33
500	7.89	90.20	74.12	63.61	68.20	60.85	71.07	65.92
600	6.20	2.39	12.07	9.53	17.20	15.84	12.74	10.58
Total weight loss	72.96	100.00	98.77	98.14	97.89	95.15	98.44	96.85

#### 4. Conclusion

The incorporation of the palm kernel shell into the LDPE had changed the thermal properties of the LDPE/PKS composites. The higher PKS loading in LDPE/PKS composites exhibited better thermal stability of the composites. The addition of the coconut oil coupling agent (COCA) had improved the thermal stability of the composites by providing better interfacial interaction. The addition of COCA as a coupling agent was better in term of providing thermal

stability to the LDPE.PKS composites compared to AA.

## 5. References

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