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Thermal analysis of high density polethylene-maple woodflour composites

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Dedicated to Dr. David Dollimore on the occasion of his 70th birthday

Abstract

To recycle waste cellulosic materials and post-consumer disposal-synthetic polymers, various composites of the high density polyethylene (HDPE) with maple woodflour have been prepared with maleic anhydride as compatibilizer and magnesium hydroxide as flame-retardant agent. The thermal behaviors of these composites in nitrogen and air have been investigated. The effects of the addition of maleic anhydride and magnesium hydroxide on the composite matrices have also been studied by TG–DTA. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: HDPE; Thermal analysis; Maple woodflour; Recycling

1. Introduction

It is reported that 41% of the total landfill weight consists of cellulosic waste [1]. The degradation of cellulosic waste is a very slow process. The reinforcement of thermoplastic polymers with woody fillers has attracted considerable interest in recent years because of the serious economic, environmental and social problems caused by the solid-waste or post-consumer disposal [2].

Methods of recycling cellulose were developed to utilize this inexpensive and abundant resource. Products derived from recycles resources use less energy than those manufactured from virgin materials. Waste wood has several major advantages over plastics, e.g., it is versatile, nontoxic and low-cost. When combined with recycled plastics, the cost of end-products will drop drastically.

Considering the potential as a fire hazard, flame retardancy is also another topic of interest and importance for the high density polyethylene (HDPE)–maple woodflour composites. Studies on the thermal degradation of a polymer in an inert atmosphere usually precede those of more complex thermal-oxidative degradation in an oxidizing environment. Information on the production of combustible volatiles, such as monomers, carbon monoxide, hydrocarbons and hydrogen, as well as non combustible gases, including carbon dioxide and water vapor, can be obtained by studying the thermal degradation of the composites.

In the present study, HDPE was chosen because it is the most popular plastic in daily life. It is readily available and easy to recycle [1]. The HDPE was mixed with the maple woodflour, a common industrial

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Table 1
Other materials used in HDPE–maple woodflour composites

Chemicals	Company	Purity (wt%)	Melting point (°C)	Boiling point (°C)
Maleic anhydride pellet	ARCOS Organics	99	52.8	202
Magnesium hydroxide	MC & B	>95	380[a]	–
Maple woodflour	American Wood Fibers	–	–	–

[a] Decompose at 380°C.

by-product. In order to establish compatibility, maleic anhydride was used as compatibilizer. In some samples, magnesium hydroxide was added as flame-retardant/heat-resistant agent.

2. Experimental section

LS 5060 HDPE pellets with diameter around 3 mm and density of 0.94 g/cm^3 were supplied by Quantum Chemical. Table 1 summarizes the other regents used in the composite.

Table 2 contains a summary of the composition of the mixtures which were subjected to the kneading process. The composite are identified in Table 2 as A, B, C, D, etc. The composite was prepared in a single screw extruder, also called Brabender extruder. The mixtures with composition in Table 2 were fed into the hopper of the extruder and emerged as a hot melt at the die. The processing temperature is set to 220°C for the feeding, middle and die zone in extruder. A batch about 100 g went through the extruder over a period of about 5 min. The hot melt composites at the die were immersed into cold water to facilitate their solidification. The extruded composites were then cut to small pieces around 10–30 mg and analyzed using the simultaneous TGA–DTA 2960 unit from TA Instruments. The samples were placed in a platinum crucible, with an empty platinum crucible as a reference. The thermal behaviors were studied using a rising temperature program at 10°C/min, in both dry air and dry nitrogen at 100 ml/min.

Table 2
Composition of starting mixtures for kneading process[a]

No.	HDPE	Maple	Maleic anhydride	Magnesium hydroxide
A	90.81	9.19	–	–
B	95.26	4.74	–	–
C	89.92	9.15	0.93	–
D	90.69	4.59	4.72	–
E	92.10	4.51	3.39	–
F	93.49	4.63	1.88	–
G	94.37	4.66	0.97	–
H	89.09	9.02	0.94	0.95
I	89.73	4.49	0.93	4.85
J	92.58	4.51	0.96	1.94
K	93.52	4.60	0.94	0.94

[a] All the numbers are in weight percentage.

3. Results and discussion

As reported, the glass transition temperature of HDPE is −20°C; the melting temperature is 130°C; the flash ignition is 340°C and the self-ignition is 350°C in air [3]. In the present study, the sample of HDPE was heated in the thermal analysis unit to obtain baseline results in both air and nitrogen. In nitrogen, the TG (wt% versus temperature) and the DTG plots, which are presented in Fig. 1(a) show depolymerization process at 498°C. The DTA plot, Fig. 1(c), shows a melting temperature at 140°C, followed by another endothermic peak at 482°C, when depolymerization occurs. The deviation of the melting temperature mainly results from the different degree of polymerization of HDPE [3]. In the air, similar endothermic peaks occur around 140°C, followed by a rather complicated DTG plot, as shown in Fig. 1(b), with corresponding exothermic peaks on the DTA plots as shown in Fig. 1(d). This pattern of behavior may be compared with other reported thermal analysis data [3].

The corresponding thermal analysis data for maple woodflour in air and nitrogen is shown in Fig. 2. As expected, there is an endothermic peak around 360°C representing thermal degradation. In air, two exothermic peaks are observed around 328°C and 447°C resulting from combustion.

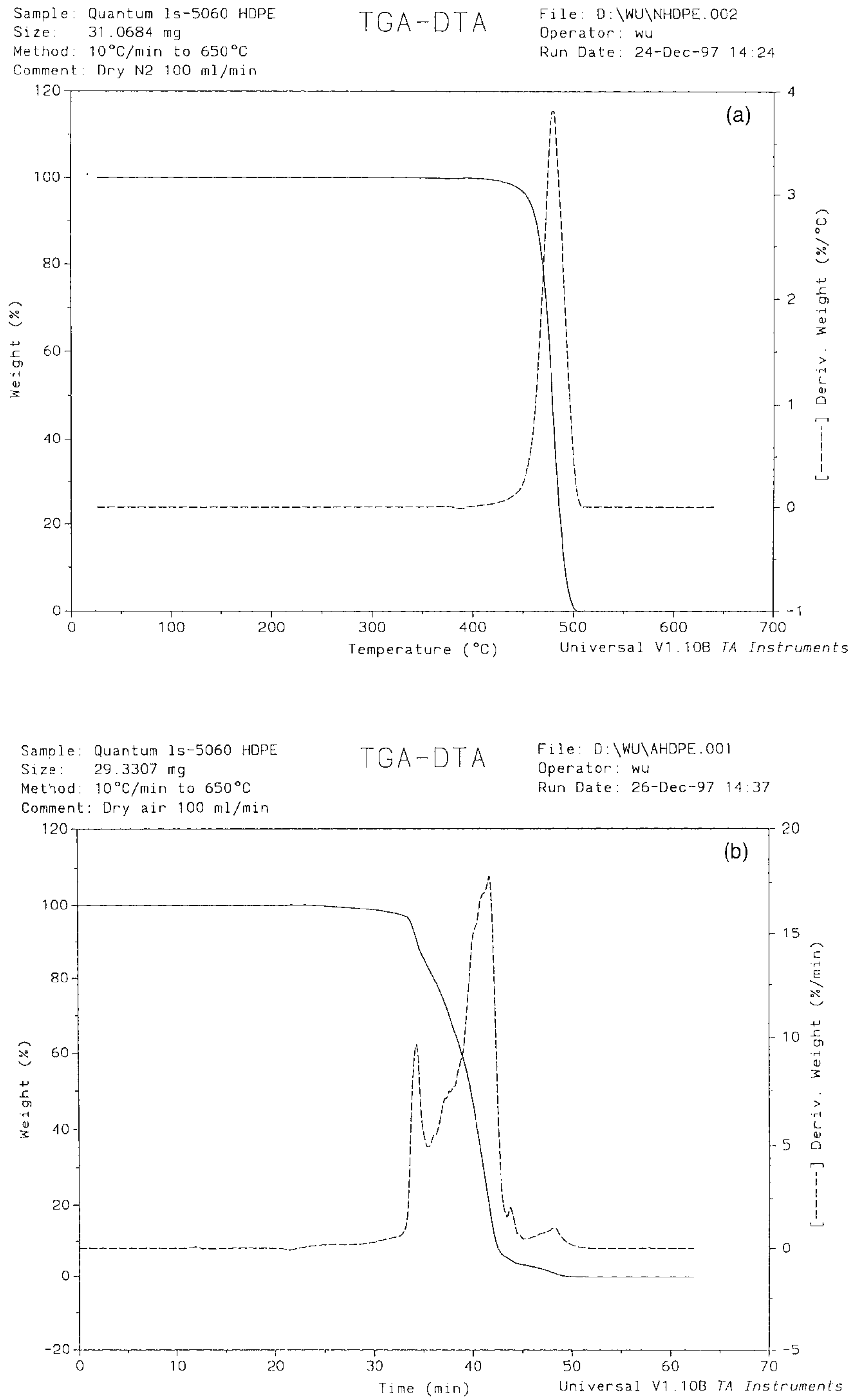
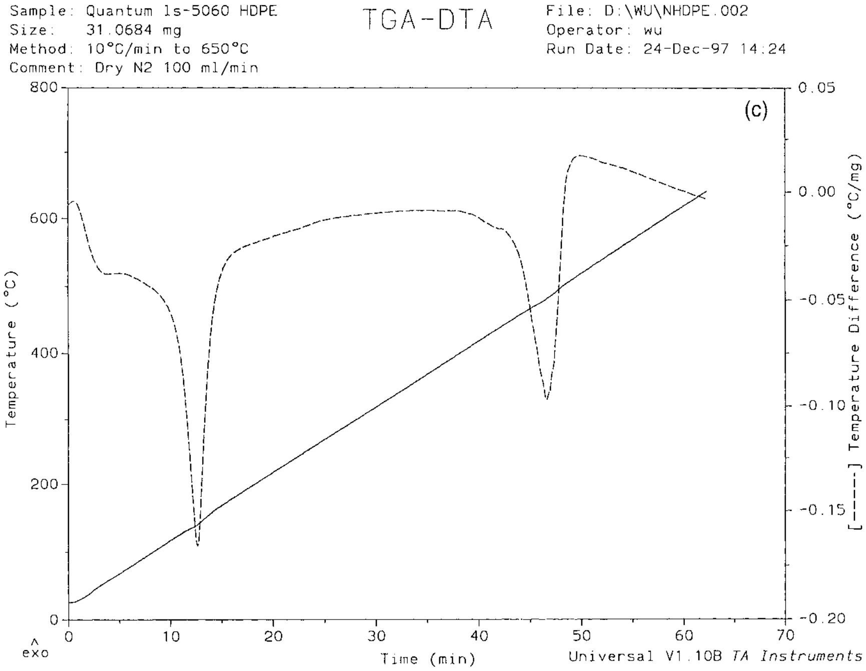


Fig. 1. TG–DTG of HDPE in (a) nitrogen and (b) air at 100 ml/min and a heating rate of 10°C/min, with the corresponding time–temperature and DTA plots in (c) and (d).



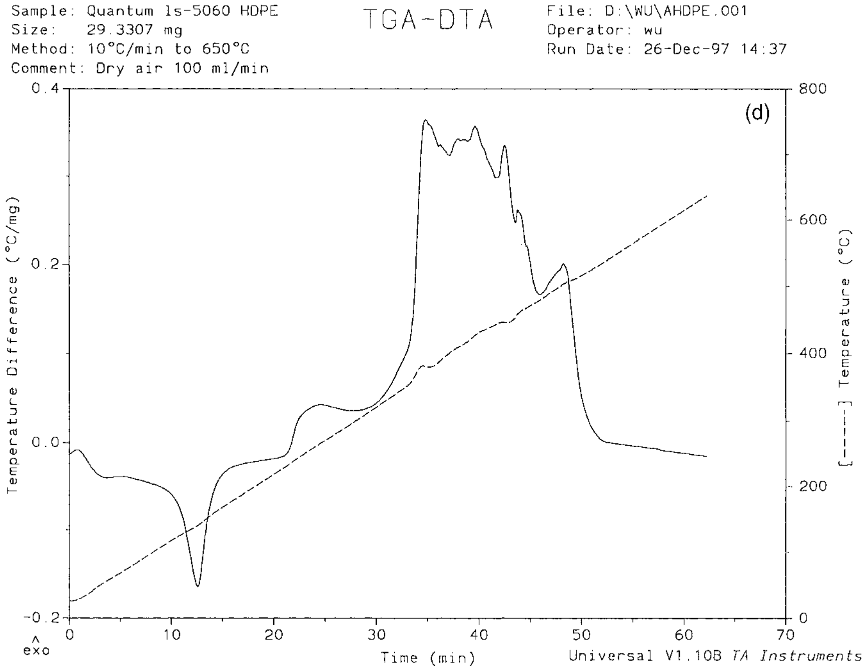


Fig. 1. (*Continued*).

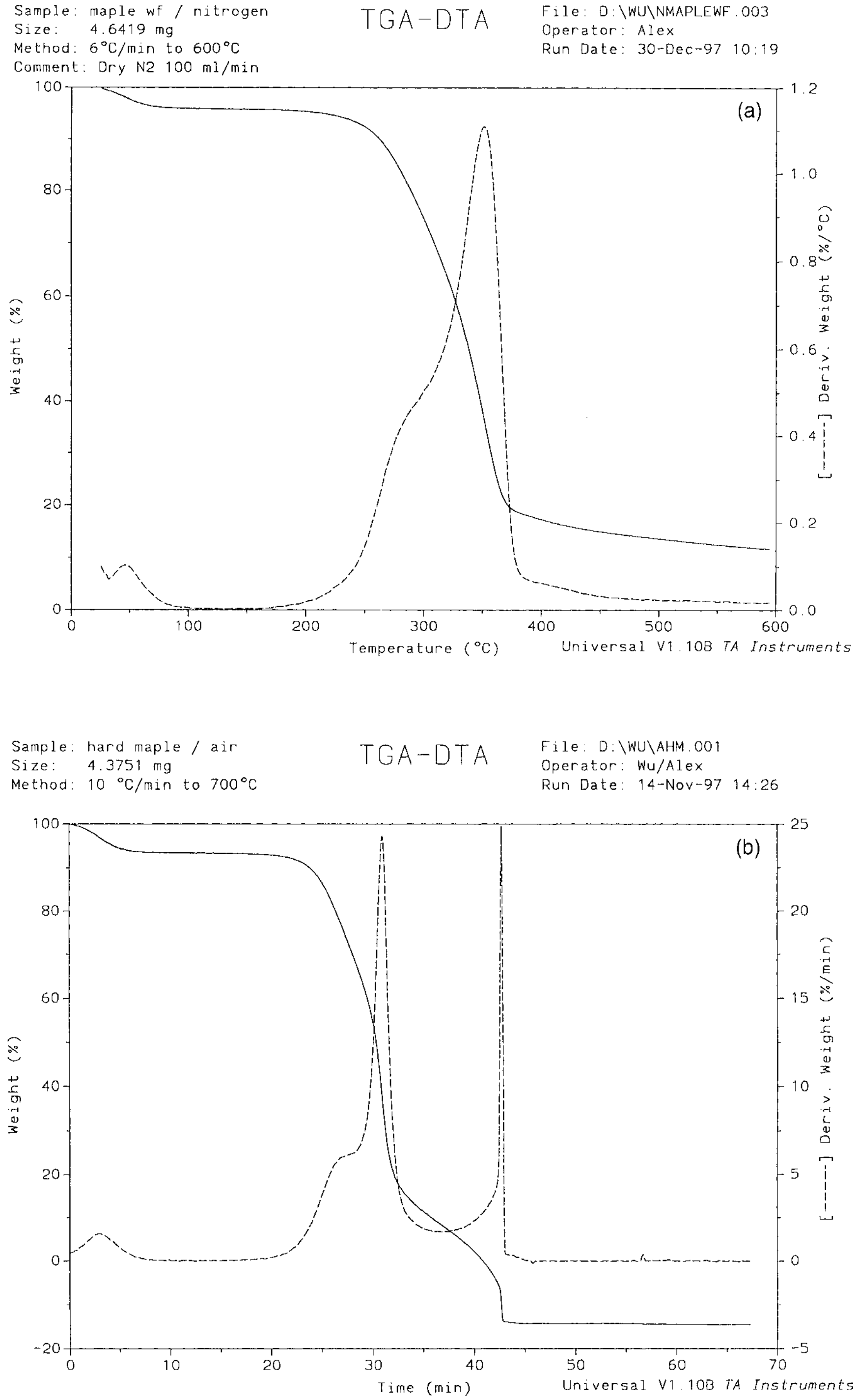
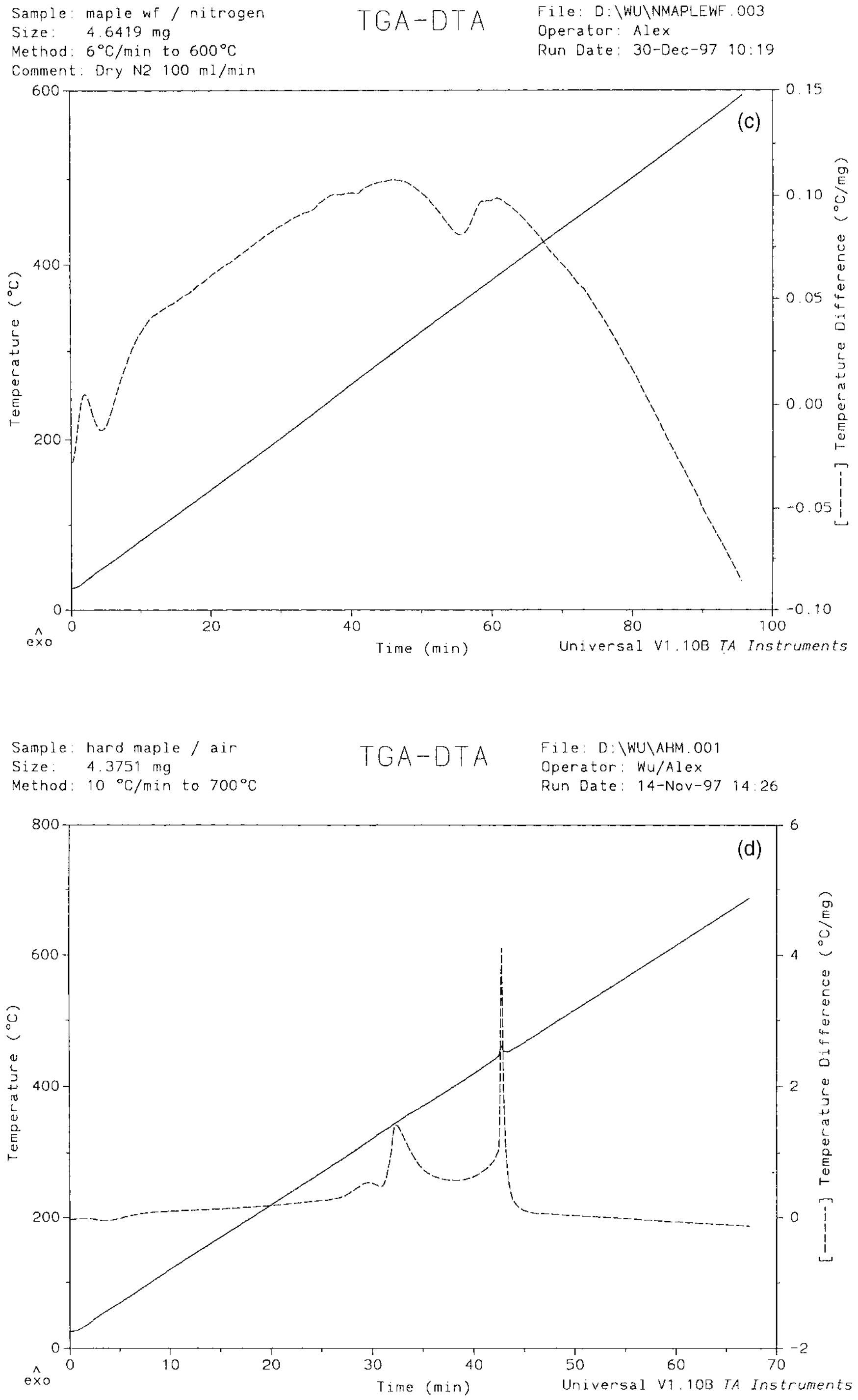


Fig. 2. TG–DTG of maple woodflour in (a) nitrogen and (b) air at 100 ml/min and a heating rate of 10°C/min, with the corresponding time–temperature and DTA plots in (c) and (d).



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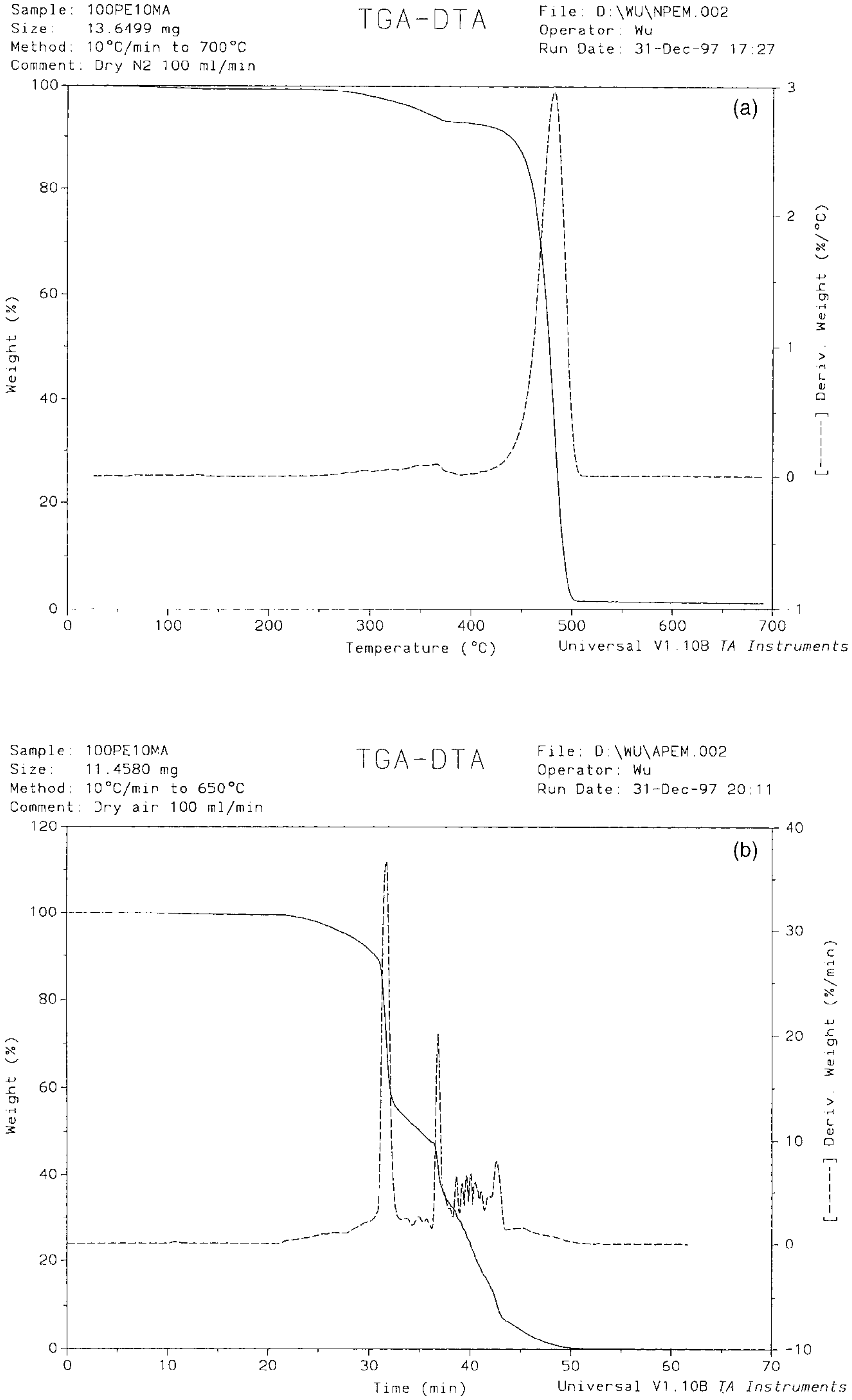


Fig. 3. TG–DTG of sample A in (a) nitrogen and (b) air at a 100 ml/min and a heating rate of 10°C/min.

Fig. 3 shows the TG and DTG plots of sample A in air and nitrogen. In comparison with Fig. 1(a), the DTG peak at 359°C arises from the addition of maple woodflour as shown in Fig. 2(b). In Fig. 3(b), the TG and DTG curves in air represent the superimposition of HDPE and maple woodflour. The first peak around 317°C mainly results from HDPE; the second peak around 368°C results from both HDPE and maple. The third peak around 427°C results only from HDPE, since in this temperature range, maple has no DTG peak. It can be concluded from Fig. 1(b) and Fig. 3(b) that the addition of maple woodflour facilitates the oxidation and combustion, since wood is more combustible than HDPE. The DTA plot of sample A is shown in Fig. 4, as compared with DTA plot of HDPE in Fig. 1(d) and that of maple woodflour in Fig. 2(d).

In nitrogen, sample B shows similar TG and DTG plots to sample A, as shown in Fig. 5(a) and Fig. 2(a). In air, the oxidation was delayed by a decreased quantity of maple, compared the pure HDPE TG–DTG, Fig. 1(b), with sample B, Fig. 5(b).

The main difference of samples C, D, E, F and G from A and B is that the former have various amount of maleic anhydride (MA) in their composition. MA provides a better interface between the matrix and wood filler improving the mechanical properties of unsaturated polyester–wood composite [5]. When the plots of sample B are compared with sample G, they are similar to HDPE and maple woodflour, except for 0.97 wt% MA in sample G. Fig. 6 shows the TG and DTG plots of sample G in nitrogen (a) and air (b). The addition of MA has minimal effect on the thermal behavior of the composites in nitrogen. Even as the quantity of MA increases, the TG–DTG plots of sample E, as shown in Fig. 7(a), does not show a significant difference from sample G. The first peak results from the melting of MA, while the second peak arises from melting of maleic acid, formed after MA adsorbs moisture from air. Beyond 200°C, there are no significant changes in TG–DTG curve of MA. The introduction of MA also does not affect the thermal behavior of the composites in air as shown in Fig. 6(b) and Fig. 7(b).

The influence of magnesium hydroxide ($Mg(OH)_2$) on the thermal behavior of the composites was also studied. Magnesium hydroxide is used as a flame retardant, whose efficiency was readily determined with thermal analysis [4]. Sample K can be compared

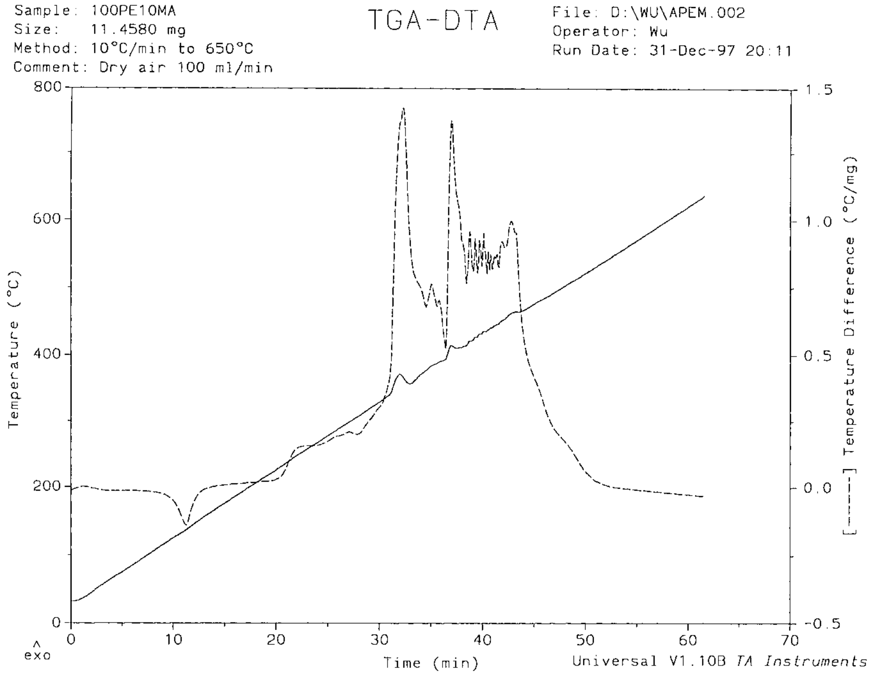


Fig. 4. DTA signals of sample A in air.

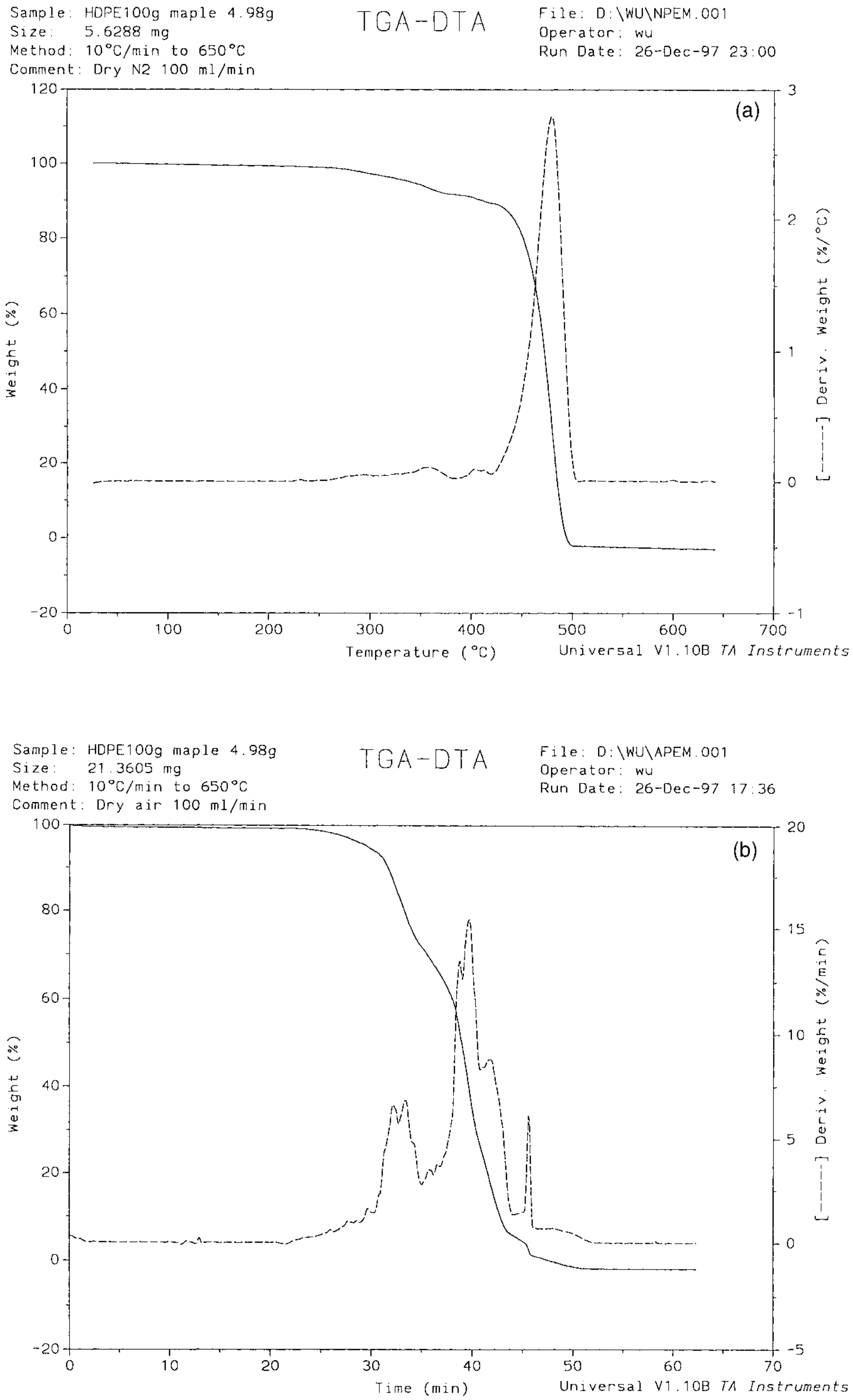
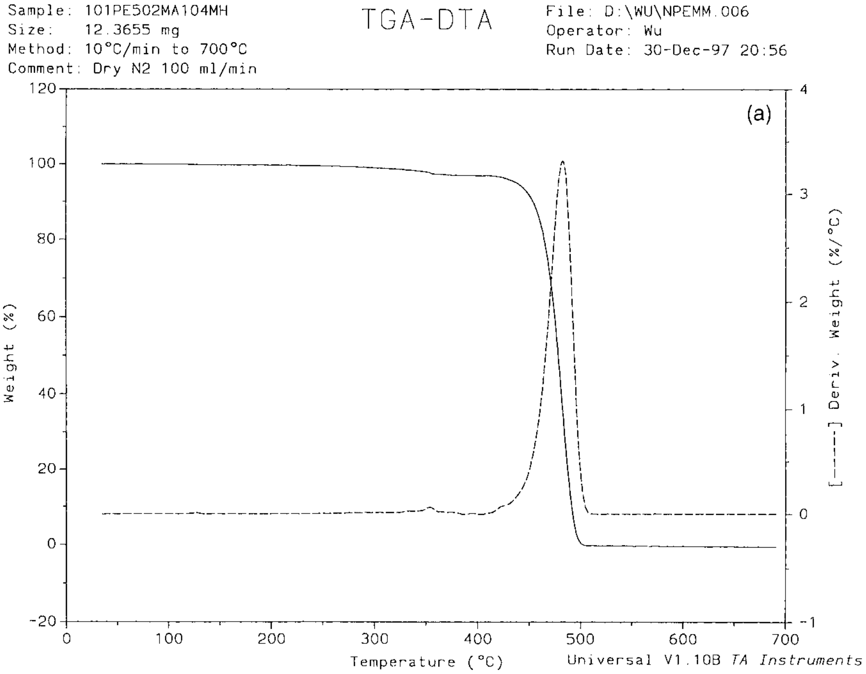


Fig. 5. TG–DTG of sample B in (a) nitrogen and (b) air at 100 ml/min and a heating rate of 10°C/min.



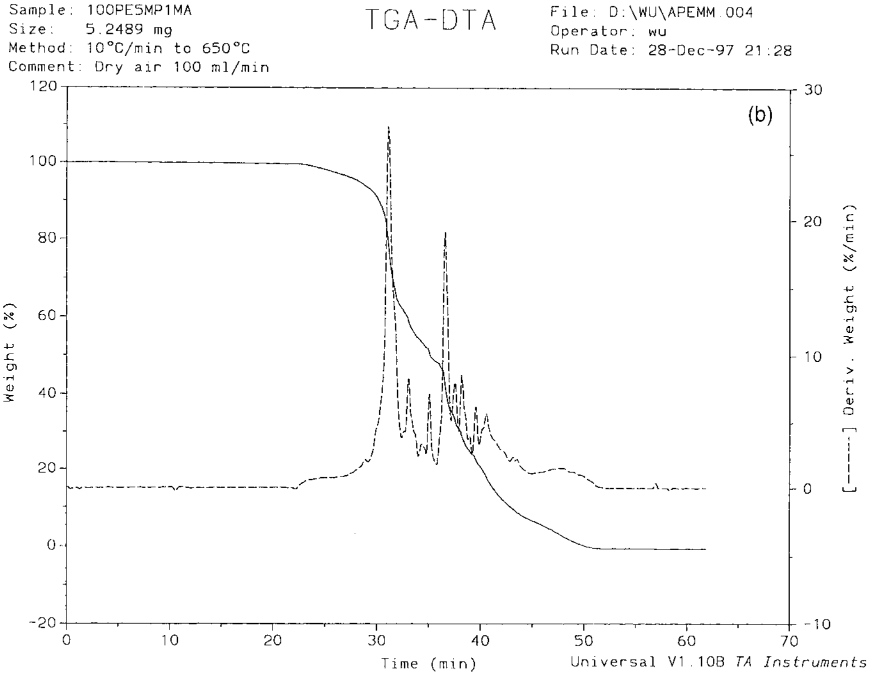


Fig. 6. TG–DTG of sample G in (a) nitrogen and (b) air at 100 ml/min and a heating rate of 10°C/min.

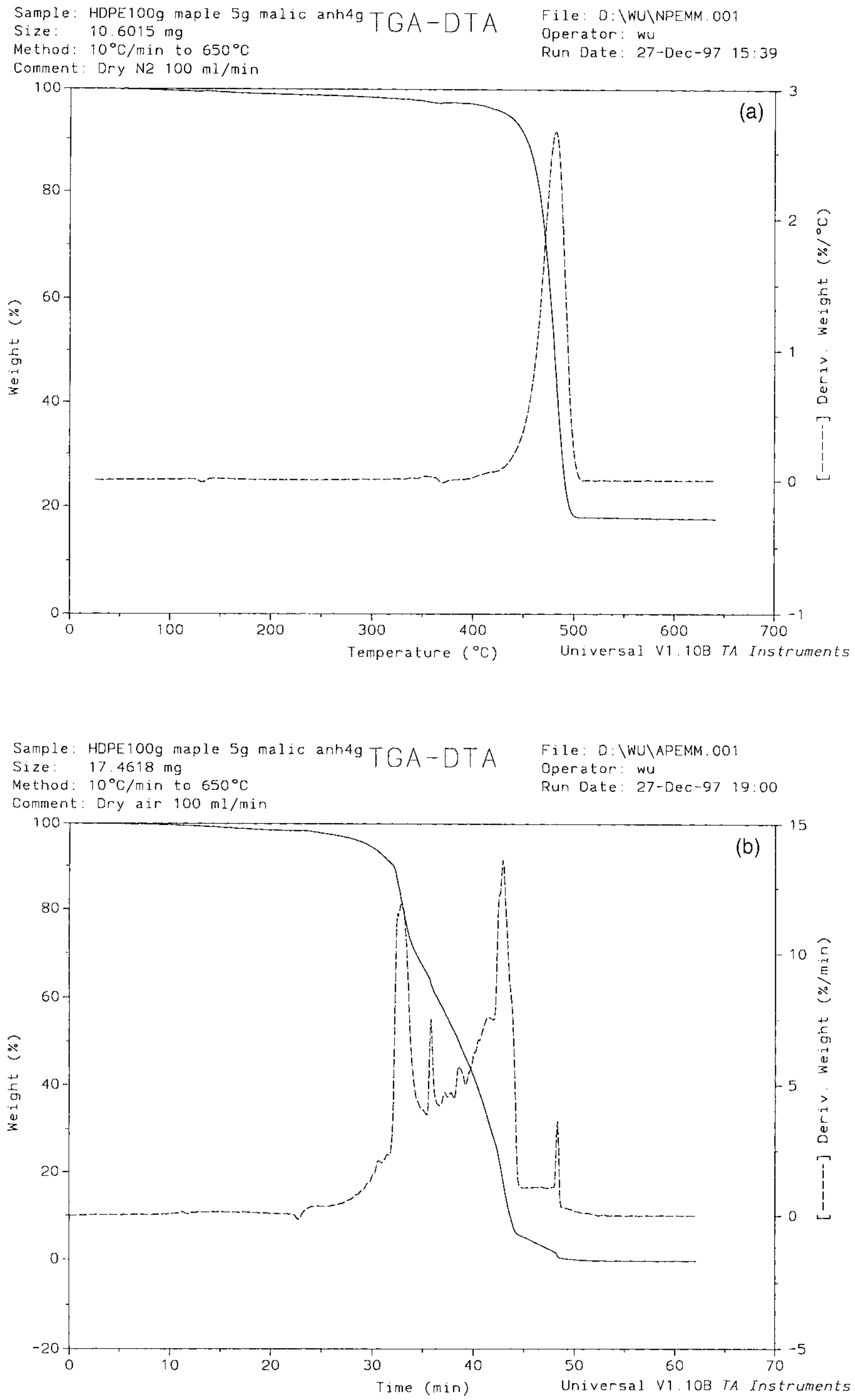


Fig. 7. TG–DTG of sample E in (a) nitrogen and (b) air at 100 ml/min and a heating rate of 10°C/min.

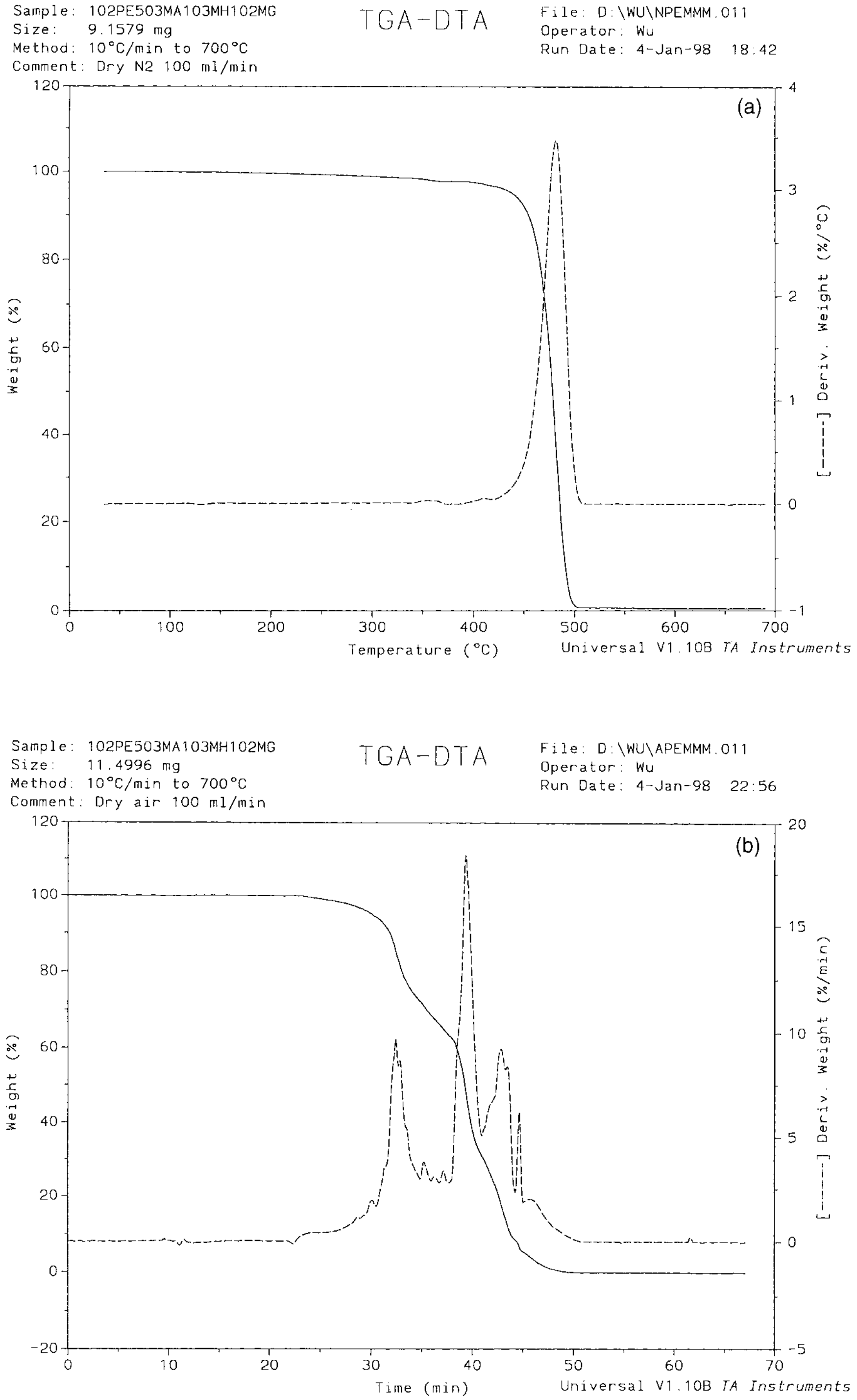


Fig. 8. TG–DTG of sample K in (a) nitrogen and (b) air at 100 ml/min and a heating rate of 10°C/min.

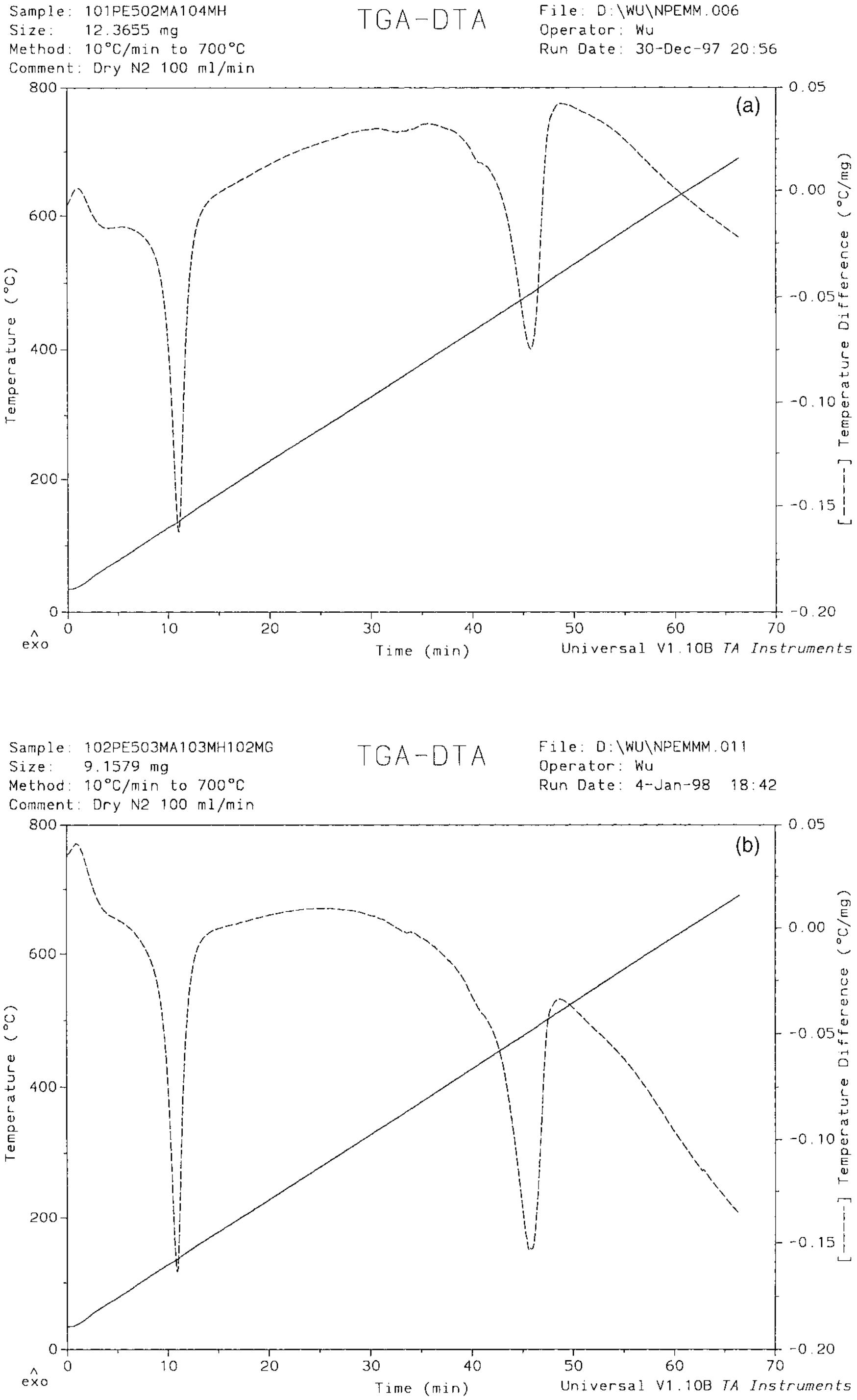


Fig. 9. DTA signals of sample G (a), K (b) and I (c) in nitrogen at 100 ml/min and a heating rate of 10°C/min.

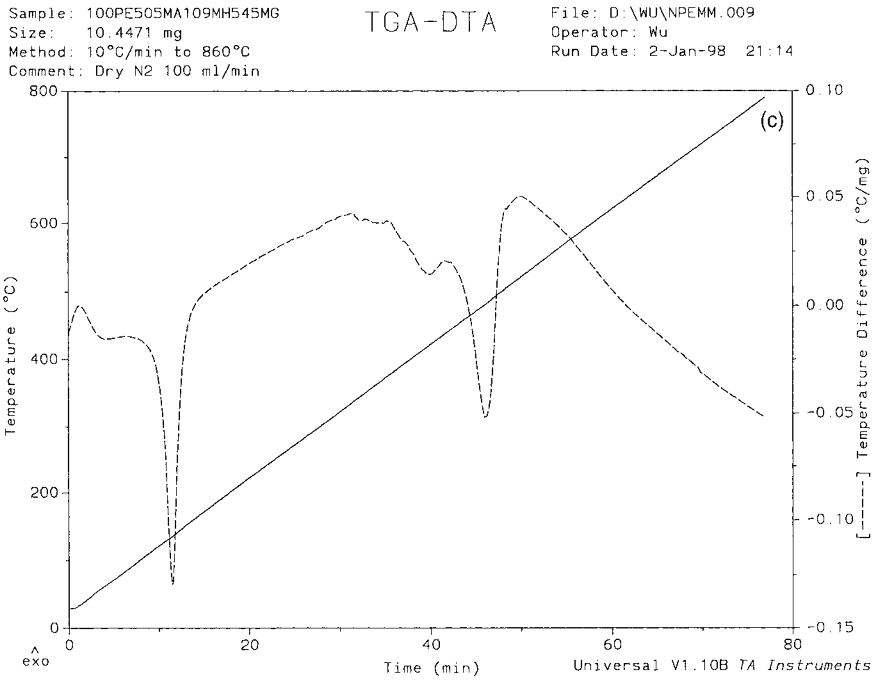


Fig. 9 (*Continued*).

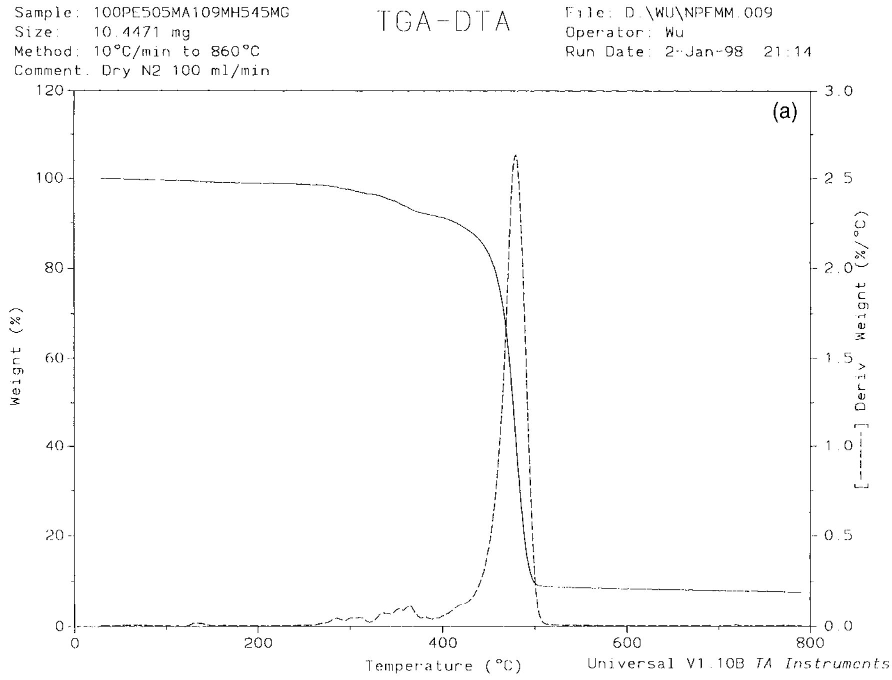


Fig. 10. TG–DTG of sample I in (a) nitrogen and (b) air at 100 ml/min and a heating rate of 10°C/min.

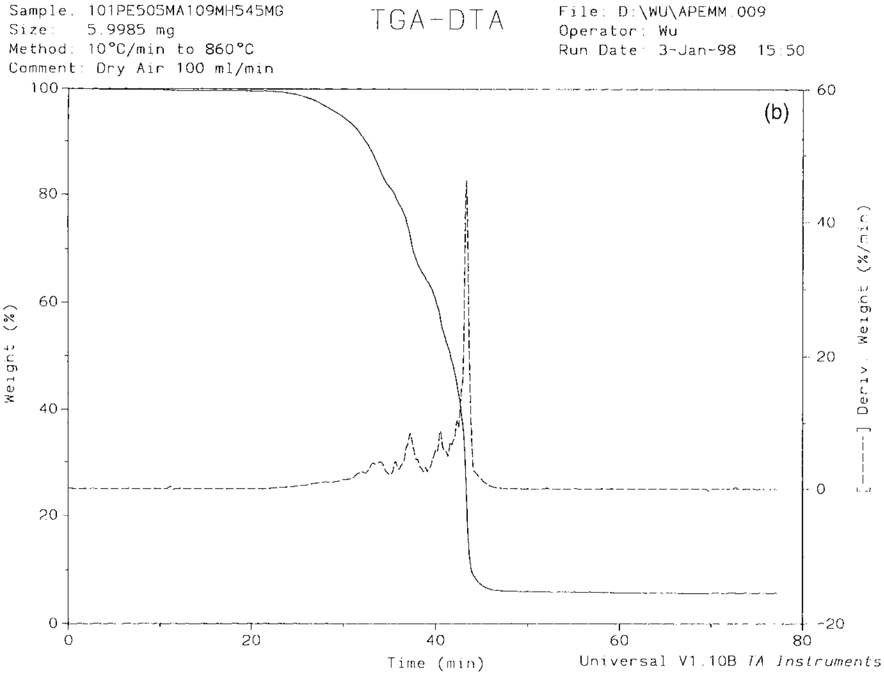


Fig. 10. (*Continued*).

with sample G, because they have similar composition except for the 0.94 wt% $Mg(OH)_2$ in sample K. There is no great difference between the TG–DTG plots, as shown in Figs. 6 and 8 Sample K has more residue, around 0.6 wt% due to the decomposition of $Mg(OH)_2$, after heat treatment. However, DTA plots show some difference, especially around 380°C, where the maximum decomposition of $Mg(OH)_2$ occurs and the shoulder of the DTA signal becomes wider, as shown in Fig. 9. If the DTA plot of sample I is compared with that of sample K, which differ by the quantity of $Mg(OH)_2$ added, there is one obvious endothermic peak around 400°C, due to addition of $Mg(OH)_2$, as shown in Fig. 9(c). The TG–DTG plot of sample I, which is shown in Fig. 10(b), in air shows flame-retardancy after the addition of $Mg(OH)_2$. There are three big peaks around 330°C, 390°C and 440°C in sample K as shown in Fig. 8(b), while sample I only has one big peak around 440°C in Fig. 10(b). The DTA plots also show a similar flame retardant effect.

The mechanism of $Mg(OH)_2$ as a flame-retardant has been described [4]. Since it decomposes, i.e., loses water around 380°C, the reaction absorbs heat and results in MgO which possesses thermal conductivity and has excellent thermal stability. Also $Mg(OH)_2$ is abundant and inexpensive.

4. Conclusion

Various composites of HDPE with maple woodflour have been prepared with the addition of the compatibilizer, maleic anhydride, and the flame-retardant agent, magnesium hydroxide. It was found that the addition of maple woodflour to the HDPE matrix facilitates its oxidation and combustion, while maleic anhydride has little effect on the thermal behaviors of composites. Magnesium hydroxide increases the flame-retardancy of the composites. The recycling of waste cellulosic materials as composites with synthetic polymers demonstrates its potential in the future.

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