

## **EFFECT OF POFA ON THERMAL STABILITY OF BENTONITE FILLED POLYPROPYLENE COMPOSITES.**

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### **ABSTRACT**

The PP composites with the presence of Palm Oil Fatty Acid Additive (POFA) were compounded using a Polydrive Thermo Haake with Rheomix R 600 for about 7 minutes. The temperature and the rotor speed used were 180°C and 50 rpm respectively. POFA was introduced in bentonite filled PP composites as a compatibiliser. The thermal stability of the composites with the presence of POFA measured by DSC show that fusion enthalpy for crystallisation ( $\Delta H_c$ ) and melting ( $\Delta H_m$ ), the melting and cooling temperature reduced as compared to control. Thermal degradation of composites which is analysed by TGA improved with the addition of POFA compared to control system (without compatibiliser).

### **INTRODUCTION**

Generally, the improvement of the interfacial bonding between the hydrophilic fillers and the hydrophobic matrix (PP) has been an important issue in the research field, because the interfacial adhesion between the filler and PP play an important role in the determining the properties of composites (1).

Therefore, to improve the compatibility between the filler and matrix, two methods were often used. One method is the modification of the filler surface using coupling agents including silane, titanate, and other, small molecular coupling agents; the other method is the modification of the matrix by grafting some small molecules with different chemical group to polyolefin chains such as acrylic acid, maleic anhydride, and acrylic esters.

Palm oil predominantly made up to triglycerides. Fatty acids obtained from palm oil processing consist of a mixture of myristic, palmitic, stearic, oleic, linoleic acid, etc. These acids are long stearic chain compounds containing an even number of carbon atom C<sub>10</sub> to C<sub>18</sub>. Palm oil fatty acids additive (POFA) has been widely used in natural rubber compound (2). In this work, the POFA is introduced as a compatibiliser. The aim of this paper is to investigate the effect of compatibiliser on thermal stability of bentonite filled PP composites. So far, there is no report on the use of this kind of fatty acids as a compatibiliser in filled thermoplastic composite. Therefore, the results of adding this kind of compatibiliser on bentonite filled PP composites were evaluated focus on thermal stability of the composites.

## **EXPERIMENTAL**

### *Materials*

The polypropylene (PP) used was a homopolymer (TITANPRO PM – 255) manufactured by Titan PP Polymers (M) Sdn. Bhd. The density and melt flow rate at 230°C of PP were 0.9 g/cm<sup>3</sup> and 1.6 g/10min respectively. The bentonite with bulk density of 0.9 g/cm<sup>3</sup> was supplied by Ipoh Ceramics Sdn. Bhd. The physical properties of bentonite were analysed using a Malvern Mastersizer. The average particle size of the bentonite and specific surface area are 23.1 µm and 0.42 sq.m/gm, respectively. The chemical analysis of bentonite has been reported in our previous paper [3]. POFA was prepared in our own lab; the synthesis procedure was reported on a previous work [4]. The amount of compatibilisers used in this study is about 2 wt % by weight of PP [5].

### *Preparation of bentonite filled polypropylene composites*

Bentonite was dried in an air oven at 105°C for 24 hours to expel moisture prior to blending with PP [6]. A mixing study was carried out using an internal mixer Polydrive Thermo Haake R600. The bentonite powder and PP granules were prepared to produce composites that have different composition, consisting of bentonite loading between 0 wt percent (control) to 50 wt percent. Mixing was carried out at a mixing temperature of 180°C with a rotor speed of 50 rpm and for a period of 7 minutes. Samples of the composites were compression moulded in an electrically heated hydraulic press model GT-7014 – A30C. The lower and upper mould temperatures were set up at 180°C with the hydraulic pressure 100 kg/cm<sup>2</sup>. Then subsequent cooling was carried out under a hydraulic pressure of 100 kg/cm<sup>2</sup> for 5 minutes.

### *Thermal analysis-DSC*

The Differential Scanning Calorimetry (DSC) measurements were performed in a Perkin-Elmer DSC 7 based on ASTM D3417. DSC calibrated with indium standard prior to use. About 10 mg of the samples were first heated from room temperature to 200°C at 40°C/min and held there for 5 min to remove the thermal history, and cooled to room temperature at 10°C/min to record the crystallisation behaviour, and then reheated to 200°C at 10°C/min to trace the melting behaviour.

### *Thermo Gravimetric Analysis (TGA)*

Thermo gravimetric analysis of the composites was carried out with a Perkin-Elmer Pyris 6 TGA analyser from 50°C to 600°C at nitrogen airflow of 50 ml/min. About 10 mg of samples were heated at 20°C/min. The change in weight with temperature was processed to display a weight vs. temperature plot.

## **RESULTS AND DISCUSSION**

### *DSC*

The most prominent effect of particulate fillers on the crystalline structure of semi-crystalline thermoplastics is their ability to work as a nucleation agent. Though there has been some debate over the effects of crystalline changes on macromechanical properties, it seems clear that by increasing crystallinity, the modulus of PP increases and the strength and deformability decrease [7]. However, the nucleation effect differs

strongly by filler type, particle size (i.e. surface area) and filler surface treatment. For examples, it has been observed that talc is active filler, affecting strongly on the crystalline morphology of PP [8]. Calcium carbonate, instead, has typically little effect on crystallinity and can be considered as inactive filler in sense of nucleation effect [9]. By modifying the surface chemistry of the filler, nucleation effect may be unaffected, increased or decreased. The effect of POFA on thermal properties of PP have also been analysed in isothermal DSC experiments. Thermal parameters such as melting temperature  $T_m$ , crystallization temperature ( $T_c$ ), the average values of crystallisation and melting entropy ( $\Delta H_c$  and  $\Delta H_m$ ) of the studied samples were analysed by isothermal crystallisation. All the results were reported in Table 1.

Table 1: Thermal parameters of the bentonite filled composites during the crystallization and melting process

Samples	$T_c(^{\circ}C)$	$\Delta H_c(J/g)$	$T_m(^{\circ}C)$	$\Delta H_m(J/g)$
PP	128.0	89.86	166.1	85.94
PP + BENTONITE	118.0	69.65	163.06	70.76
PP + BENTONITE + POFA	113.0	67.02	161.73	65.72

In this work, details of the thermogramme obtained for various composition of PP, PP filled bentonite, PP filled bentonite with POFA are shown in Figures 2 (a) and (b). DSC scanning was carried out in the temperature range between 50 to 200°C corresponding to melting point of PP (160 – 170°C). Comparing with pure PP, the bentonite filled PP composites have lower crystallisation and melting temperatures, lower crystallisation enthalpy and heat fusion, and narrower and sharper exothermic and endothermic peaks. Careful examination on DSC curves, however reminds one that the curves have been normalised only in term of initial masses of samples tested and not in term of actual PP weight of sample. Among the bentonite filled composites, the addition of POFA has a significant effect on decreasing the crystallisation and melting temperature (Table 1). Judging from the decreasing height of the peaks for compatibilised bentonite filled PP as compared to control; it appears that incorporation of POFA reduces the level of crystallinity of PP. Slower crystallisation rate of compatibilised bentonite filled PP is observed by broadening of the crystallization peak and reduction of the melting point. Other reason for the reduction of the melting temperatures of all compatibilised bentonite filled PP systems should be attributed to the disturbance of crystalline formation induced by the bentonite in the system during cooling process. Precisely, the presences of POFA in bentonite filled PP composites can acts as a plasticizer which increased the elasticity of the chain in the composite thus, reduce the melting and crystallisation temperature. In a filler-polymer system, the crystalline structure of the matrix can be remarkable affected by the addition of filler. The percentage of crystallinity was reduced with the addition of bentonite. This mean that the bentonite did not acts as a nucleating agent in this system. Nucleating effect and induced orientation associated by the addition of filler is the factors to be considered and at this stage, the present of POFA seem to reduce the crystallisation process in bentonite filled PP composites.

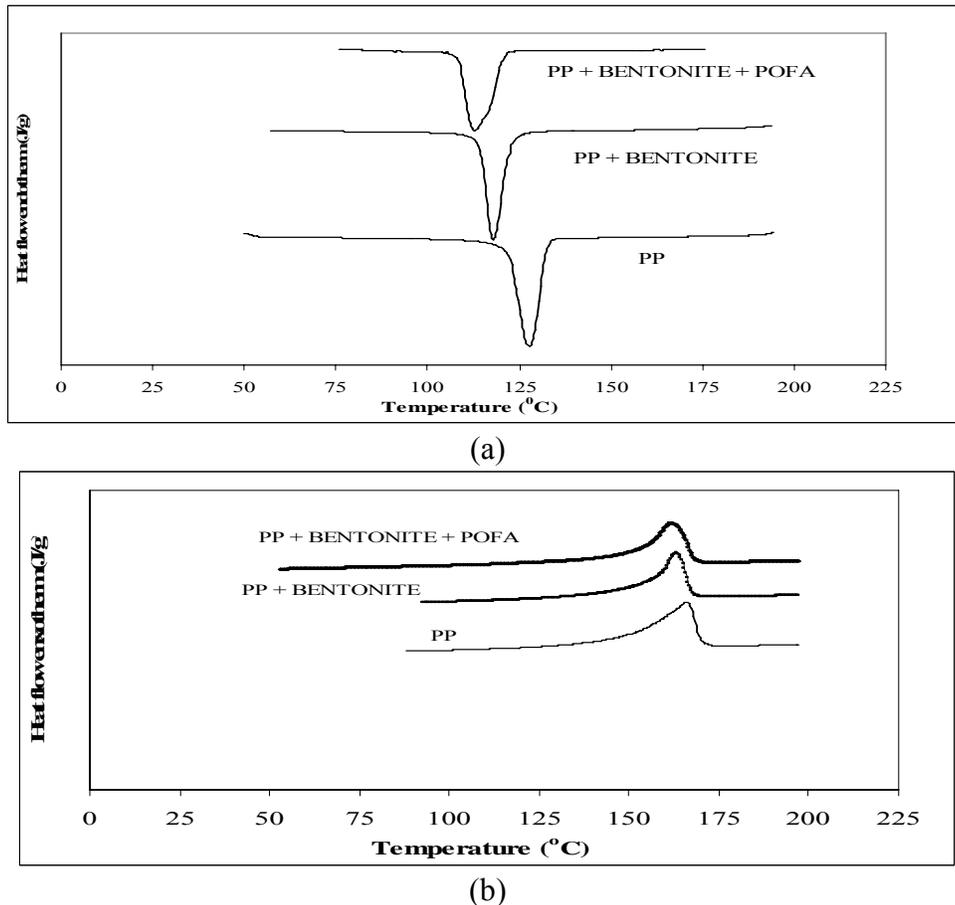


Figure 1: DSC scans of bentonite filled PP composites: (a) the first cooling scan; (b) the second heating scan.

### **TGA**

The thermogravimetric analysis (TGA) is a standard procedure in which changes in the weight of a specimen is monitored as the specimen is progressively heated. The sample weight is continuously monitored as the temperature is steadily increased. Summary of TGA experimental results for the bentonite filled composites are shown in Table 2 and Figure 2.

Table 2: Effect of compatibilisers on the thermogravimetric analysis of the bentonite filled PP composites

Samples	Initial degradation temperature (°C)	End Degradation temperature (°C)	Total weight loss (%)
PP	297.57	457.25	0.078
PP + BENTONITE	74.57	637.19	20.80
PP + BENTONITE + POFA	96.52	637.79	21.27

In the case of bentonite, the initial weight loss was 5.46% around 100.0°C and the following degradation was at the onset temperature of 582.81°C with the total weight loss values of 95.38%. Correspondingly, from the TGA experimental data and chemical analysis of bentonite [3], it can be concluded that the moisture content of bentonite was 5.46%, and the content of inorganic and organic materials were 89.92% and 4.62% respectively. From the thermal degradation curves in the Figure 2, the initial degradation temperature for PP was 297.57°C. Generally, the addition of bentonite into PP decreased the initial degradation temperature to 74.57°C. However, with the incorporation of POFA into bentonite filled PP composites the initial degradation temperature was increased to 96.52°C. The end degradation temperature of PP was 457.25°C. The incorporation of bentonite into PP was improved the end degradation temperature to 637.19°C. The presence of metal oxides in bentonite such as silica, aluminium, ferum and magnesium were attributed to this improvement. With the addition of POFA the end degradation temperature was improved further to 637.79°C. In this point of view, it can be concluded that the thermal stability of bentonite filled PP composites was improved with the addition of POFA.

## CONCLUSIONS

- From DSC thermogrammes obtained in this study, fusion enthalpy for both crystallisation ( $\Delta H_c$ ) and melting ( $\Delta H_m$ ) processes of composites with POFA have significantly reduced as compared to control. The melting and cooling temperature also reduced as POFA are added into bentonite filled PP. Therefore, it can be explained that the crystallinity of PP decreased with the present of POFA.
- The thermal stability of bentonite filled PP composites was improved with the addition of POFA.

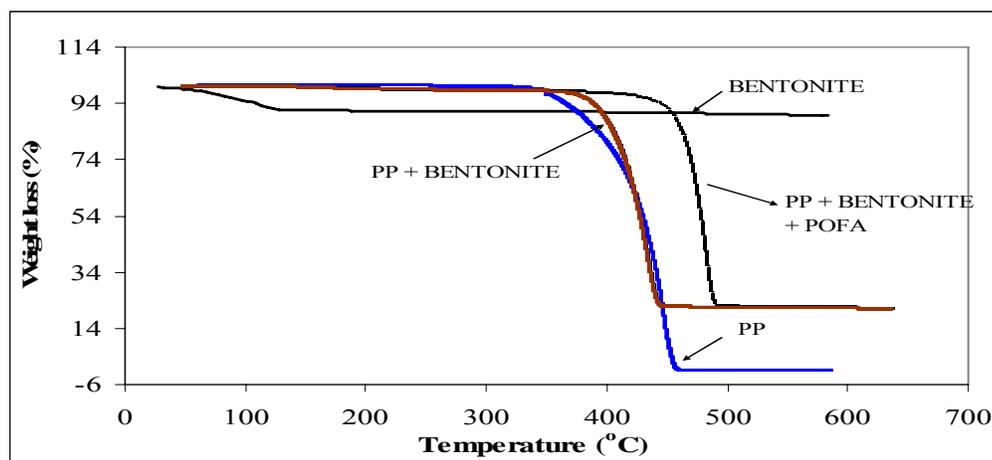


Figure 2: Thermogravimetric analysis of bentonite filled PP composites

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