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THE COMBINED EFFECT OF ORGANIC PHOSPHINATE BASED FLAME RETARDANT AND ZINC BORATE ON THE FIRE BEHAVIOUR OF POLY(BUTYLENE TEREPHTHALATE)

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ABSTRACT

Neat poly(butylene terephthalate) is highly combustible. It is not self-extinguishing, and after ignition it burns with dripping. To meet the fire safety requirements, it should be rendered flame retardant. The most common flame retardants for PBT are based on halogenated (most often brominated) or phosphorus compounds**.** Although their efficiency is lower than halogen based flame retardants, expensive phosphorus based flame retardants for polyester are preferred, because of low smoke generation, nontoxicity and low corrosion properties. Zinc borate has been widely used with other flame retardants in wood products and in several polymers. In this work the fire behaviour of zinc borate, organic phosphinate (diethyl phosphinic acid) (DPA) and zinc borate/organic phosphinate combination doped poly(butylene terephthalate) was investigated. Firstly, the mean particle size of zinc borate ($2ZnO.3B_2O_3.3.5H_2O$) powders were reduced by attrition milling. Samples were produced by twin screw micro compounder. The fire properties of the ZnB, DPA and ZnB/DPA doped PBT were investigated and compared to each other by LOI and thermal analysis. LOI values of ZnB/PBT samples were found very low even with higher filling content. At higher loading of ZnB, the dripping of the sample strongly decreased and char residue increased. It was seen that organic phosphinate acid based additives DPA is particularly effective with PBT. It was found that the combination of DPA and ZnB can be used to increase the char residue and decrease the melt dripping of PBT.

Keywords: Flame retardant, Zinc borate, Organic phosphinate, Diethyl phosphinic acid, PBT

1. INTRODUCTION

Poly(butylene terephthalate) (PBT) is an aromatic polyester. It differs slightly from PET in chemical composition but more substantially in its properties such as higher crystallisation rate and lower melting point (225 °C). High dimensional stability, tensile strength and low moisture adsorption properties are the main advantages of PBT. Therefore, it is preferred for the production of engineering plastic applications such as electronic products and automotive parts. Additionally, PBT fibres are used in carpets, sportswear, underwear and hosiery. Neat PBT is highly combustible. It is not self-extinguishing, and after ignition it burns with dripping. To meet the fire safety requirements, it should be rendered flame retardant. Commercial flame retardants for thermoplastic polyesters including PET and PBT as the moulding resin and textile products are reviewed in detail by Weil and Levchik [1]. The most common flame retardants for PBT are based on halogenated (most often brominated) or phosphorus compounds [2]. Phosphine oxides, phosphinates, phosphonates, phosphates and phosphorus-nitrogen compounds have been studied in PBT [3]. On the other hand, as a result of environmental concerns, halogen free flame retardants have become more popular. Most of the common halogen-free flame retardant systems are mainly phosphorus based products [3-5]. Although their efficiency is lower than halogen based flame retardants, expensive phosphorus based flame retardants for polyester are preferred, because of low smoke generation, nontoxicity and low corrosion properties [6-8]. On the other hand, melt dripping of polyester during burning is still a major problem. Therefore, flame retardants for PBT which promote char formation and reduce melt-dripping behaviour are still required [9, 10]. The melt dripping behaviour of different commercial flame retardants in PBT has been

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investigated and it was found that the melt flow and dripping behaviour of polymer were highly dependent on the flame retardant, mode of action and type of additive [11].

Inorganic additives such as metal oxides can change the interaction of phosphorus containing flame retardants with their chemical surroundings during pyrolysis. It means that combination of some flame retardants with phosphorus based flame retardants can optimize the effect of flame retardant agent. Various metal compounds, borates, inorganic fillers can be used as synergist with phosphorus based flame retardants [12]. Endothermic thermal decomposition of metal hydroxide, carbonate and boron additives produces non-combustible gases, such as H_2O and CO_2 diluting the oxygen supply and fuel concentration [13]. Zinc borate has been widely used with other flame retardants in wood products and in several polymers such as EVA, PVC, polyamide and polyolefin as a flame retardant, smoke suppressant, afterglow suppressant, anti-tracking agent and antibacterial agent [14, 15]. Zinc borate with a chemical formula of $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$ is stable up to >290°C and complete dehydration requires 445 J/g. So it is widely selected for polymer applications [16]. Agrawal et.al. [17] used zinc borate successfully as a flame retardant for PET, moreover they investigated that flame retardant features presented by zinc borate could further be enhanced when it is used in combination with antimony trioxide. Bourbigot et.al. [15] found out that the use of fine zinc borate particles in EVA/ATH system provided a better dispersion as the B_2O_3/ZnO glass formed by the degradation of zinc borate were homogenously distributed in polymer matrix. Wu et.al. [18] treated low-density polyethylene (LDPE) with intumescent flame retardant (APP) and ultrafine zinc borate. Ultrafine zinc borate improved the flame retardancy of LDPE and increased the residual char.

In this work zinc borate, organic phosphinate (diethyl phosphinic acid) based flame retardant powder and their mixtures doped to poly(butylene terephthalate) (PBT) in different ratios and the fire behaviour of the samples was investigated. Firstly, the mean particle size of zinc borate ($2ZnO.3B_2O_3.3.5H_2O$) powders were reduced by attrition milling. The fire behaviour of the samples was examined by limiting oxygen index (LOI) test and thermogravimetric analysis. Surface morphologies of the samples were observed by scanning electron microscopy (SEM).

2. MATERIALS AND METHODS

2.1. Materials

All starting materials were commercially available and were used without further purification. PBT in powder form was obtained from KORTEKS/Bursa. Organic phosphinate based flame retardant powder was supplied by Avocet Dye and Chemical Company/England under commercial name of CETAFLAM AD400 (DPA). It is based on diethyl phosphinic acid and zinc salt. Phosphorus content of the powder is 20%. Zinc borate (ZnB) powders ($2ZnO.3B_2O_3.3.5H_2O$) were provided by Grate Lake Chemicals Corporation/USA under commercial name of ZB-467. Some chemical and physical properties of ZnB are given in Table 1.

Table 1. Chemical and physical properties of ZnB

Physical appearance	White powder
Bulk density (25 °C, g/ml)	2.74
Mean particle size (micron)	9.6
Density (gr/cm^3)	0.469
Solubility in water (g/100 ml)	0.1
ZnO (%)	37.4
Boric acid (%)	48.1
Water (%)	14.5

2.2. Size Reduction of ZnB

ZnB powders were processed in the attritor mill to reduce the particle size of the powders from micron size to submicron scale. Stabilizers such as surfactants, ligands or polymers having functional groups such as thiol (–SH), cyano (–CN), carboxyl (–COOH), amino ($–NH_2$) can be used for prevent the particles from agglomeration [19]. Ethylene glycol (EG), Polyethylene glycol (PEG 1000), polyvinyl pyrrolidone (PVP), aluminium sulphate-18 hydrate ($Al_2O_{12}S_3.18H_2O$) (AS), sodium silicate (SS) and tri-sodium citrate di-hydrate (TSS) were used in different ratios as stabilizing agent. Particle size of the samples was measured by Malvern Zetasizer NANOZS 3600. Selected dispersion was processed in high shear fluid processor. Water was removed by rotary evaporation (Heidolph Hei-VAP).

2.3. Preparation of Flame Retardant / PBT Composites

Samples were prepared by adding 10 wt%, 20 wt% and 30 wt% zinc borate and DAP to PBT in order to investigate their individual effects on the flammability. PBT powders and flame retardant powders were mixed for twenty minutes with mechanical stirring before processing. Polyesters, when heated above their melting temperatures, tend to evaporate and show low charring behaviour due to low cross-linking. Therefore, the amount of flame retardant to be used in polyester should be minimized in order to preserve its high strength, dyeability and aesthetic characteristics. For instance the amount of flame retardant additives or comonomers must not exceed 10 wt% in textile applications [20]. Zinc borate and DAP were mixed at various ratios as the total amount of additives were maintained at 10 wt%, the compositions of the samples are shown in Table 2.

They were processed by a twin screw micro compounder (DSM Xplore) at 250 °C and moulded by microinjection device (DSM Xplore). Bar-shaped specimens (80x10x4 mm) were prepared for the Limit Oxygen Index (LOI) tests. The neat PBT was treated in the same way.

Table 2. PBT/flame retardant compositions

	Weight percent (%)		
Material	**U1**	**U2**	**U3**
DPA	2.5	5.0	7.5
ZnB	7.5	5.0	2.5
PBT	90	90	90
Total (%)	100	100	100

2.4. Characterization Tests

The crystal structure of ZnB was investigated by X-Ray Diffractometer (XRD, Rigaku-Rint 2200). The samples were exposed to CuKα radiation (λ = 1.5418 Å). Scans were performed from $2\theta=10$ to 50^o at 2 ^{o}/min scanning rate. The particle size and surface potential of milled zinc borate were measured by Malvern NanoZS 2000. 0.25 ml of the zinc borate dispersion was added to 100 ml distilled water and the pH of this diluted dispersion is maintained at 7. Zeta potential measurement was performed according to electrophoresis procedure at room temperature. Thermogravimetric analysis (TGA) were using a Setaram, Labys TG-DTA/DSC and SDT Q6000 (TA Instruments) equipment. Analysis were performed under nitrogen at a heating rate of 10 °C/min from ambient temperature to 800 °C. The thermal properties of the samples were investigated and compared using the thermograms. The flammability of flame retardant/PBT composites was tested by limit oxygen index (LOI) test device (Dynsco) according to ASTM D2863-00 standard. This test is used to determine the minimum concentration of oxygen in a mixture of oxygen and nitrogen that maintains the combustion of the sample placed in vertical position. The surface morphologies of flame retardant powders and PBT samples were investigated by scanning electron microscopy (SEM, Zeiss Evo 50EP).

3. RESULTS AND DISCUSSION

The XRD plot of zinc borate is shown in Figure 1. The plot confirms the chemical formula of the zinc borate as $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$. The particle size of zinc borate was calculated as 9.6 µm. SEM images of ZnB powders presented in Figure 2 confirmed the particle size measurement test results.

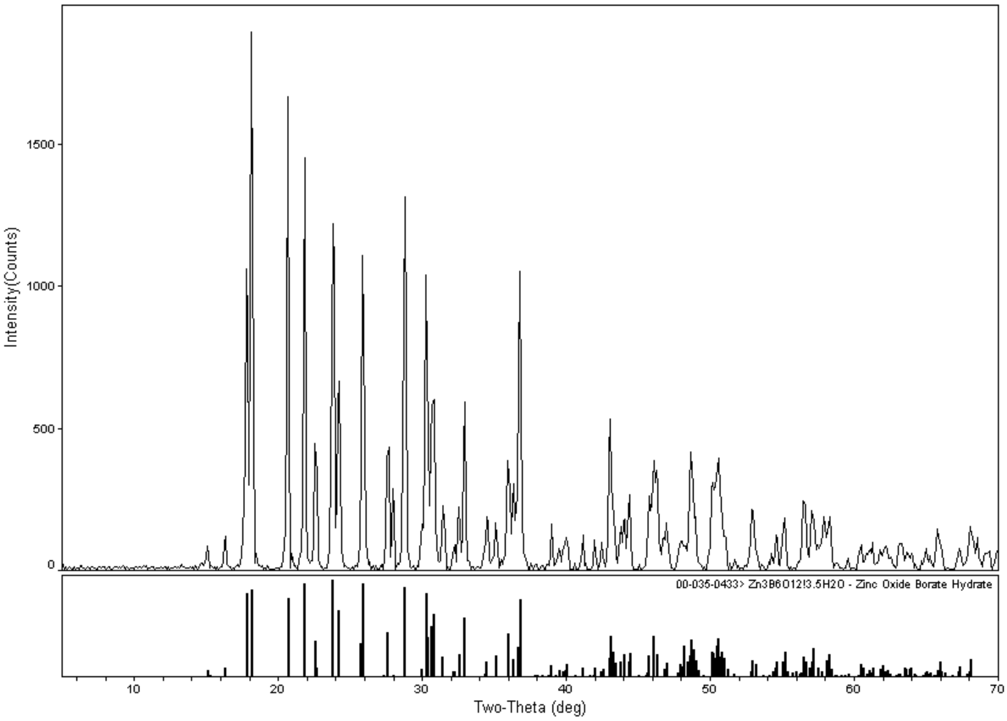

Figure 1. XRD pattern of ZnB

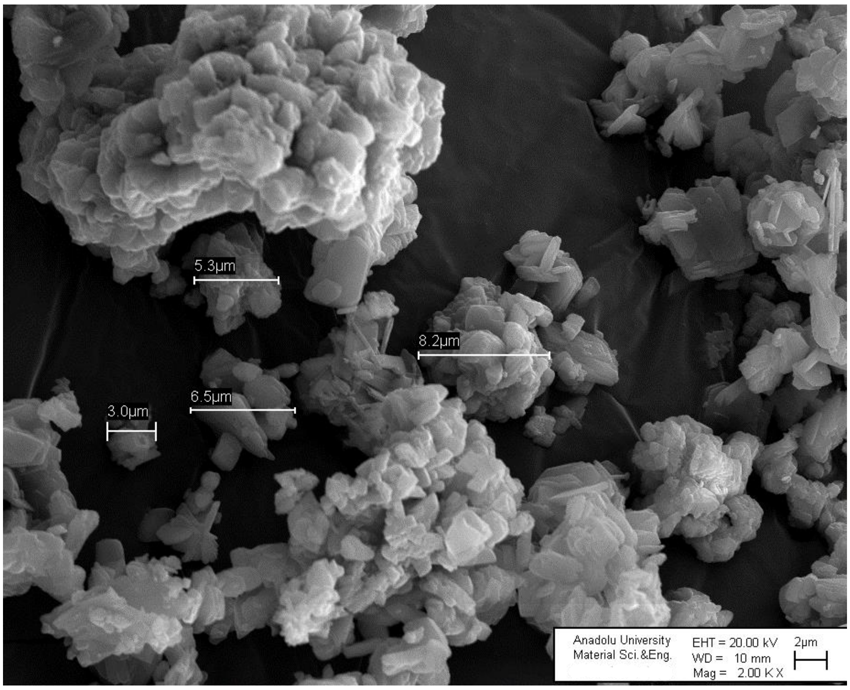

Figure 2. SEM image of ZnB powders (2.000X)

TGA, DSC and DTA plots of ZnB are shown in Figure 3. The mass loss of ZnB starts at about 300°C which is due of the loss of dehydration water. The mass loss was measured as approximately 10.4 wt% between 300-420°C and 13.80 wt% between 30-600°C. The first endothermic reaction was observed at approximately 90 °C due to the moisture and the second endothermic reaction started at about 300 °C. Other endothermic reactions were identified within the range of 350-421 °C. The maximum of main mass loss was observed at 400 °C (1.72%/min) and 419 °C (1.76%/min). It was reported that in the range of 600-700 °C zinc borate is mainly low temperature type α-$ZnO\cdot B_2O_3$, at 700-900 °C α-$ZnO\cdot B_2O_3$ and β-$ZnO\cdot B_2O_3$ coexist in equilibrium [21]. Endothermic peaks at 860 °C and 970 °C indicate the melting of α-$ZnO\cdot B_2O_3$ and β-$ZnO\cdot B_2O_3$, respectively.

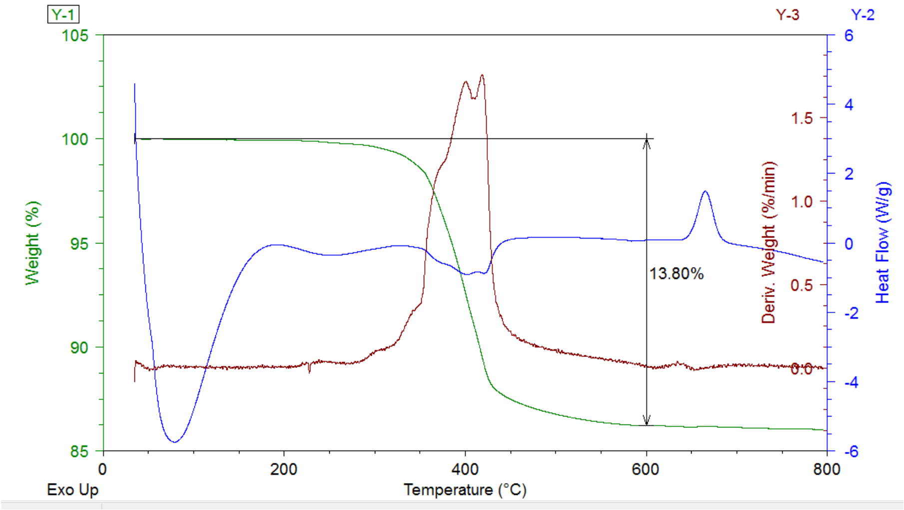

Figure 3. Thermal analysis test results of DAP

TGA, DSC and DTA plots of DAP are shown in Figure 3. DAP decomposed in single step between 350 °C and 550 °C with a maximum of weight loss at 469 °C. During the main decomposition step phosphinate compounds release in gas phase [22]. A residue of 18 wt.% remained at 600 °C, which represents the zinc compound and phosphorus content in the DAP.

3.1. Particle Size Reduction of Zinc Borate Powders

ZnB powders were wet-milled in attritor mill to reduce the particle size. The attrition milling studies were conducted using six different stabilizing agents. Ethylene glycol, aluminium sulphate and polyvinyl pyrrolidone failed to contribute to the size reduction of powders to sub-micron scale when used as stabilizing agents. Moreover, the zeta potential values of dispersions were measured as approximately zero. Therefore, the milling processes were conducted using polyethylene glycol (PEG1000), sodium silicate (SS) or tri-sodium citrate di-hydrate. The results of zeta potential and particle size measurements are shown in Table 3. The particle size of powders was successfully reduced to sub-micron scale using any of these three stabilizing agents. However, TSS has significantly contributed to the zeta potential value. The tendency of agglomeration of particles increase as the zeta potential approaches 0 from -30. When 2.21 g of TSS was used, the particle size was reduced to sub-micron scale, moreover the zeta potential value was maintained at an acceptable level, thus, this dispersion composition was chosen for further studies.

In order to further reduce the particle, size the dispersion was then processed in high shear stress processor (Microfluidics, M110P). The particle size of the powder after this process was measured as 498.1 nm. The SEM image of this powder is shown in Figure 4. Despite their agglomeration a major portion of powders have a particle size below 1 µm.

Table 3. Particle size and zeta potential test results of ZnB after attrition milling

Stabilizing Agent	Quantity (g)	Mean particle size (nm)	Zeta Potential (mV)
PEG 1000	0.50	874.1	-17.4
	1.00	1.008.0	-18.4
	1.25	829.1	-31.7
	2.00	1.172.9	-36.8
SS	0.31	828.3	-10.2
	0.52	823.1	-15.8
	0.62	862.7	-6.67
	0.96	719.9	-6.63
	1.06	1.147.0	-9.83
TSS	1.49	758.0	-35.3
	2.21	772.2	-48.6
	2.94	1.220.0	-63.5
	3.68	1.381.0	-64.8

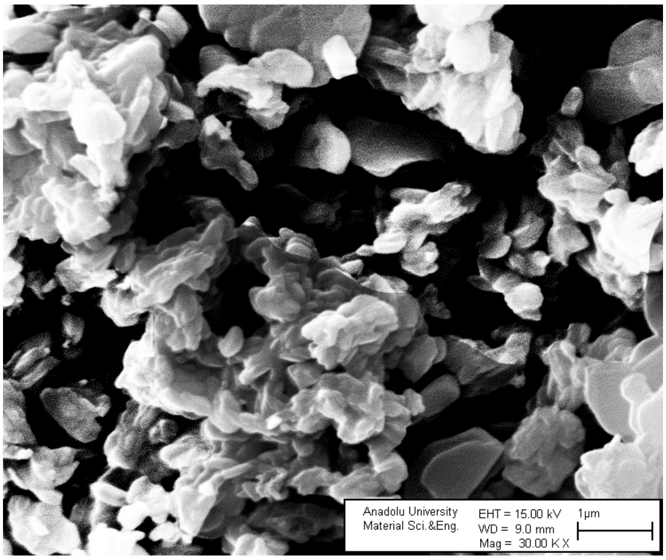

Figure 4. SEM image of ZnB particles after the attrition milling (30.000 X)

3.2. LOI Test Results

LOI test results of PBT samples flame retarded using DPA, ZnB and ZnB/DPA are shown in Table 4. DPA is concluded to be a good flame retardant for PBT as the LOI of PBT increased to 29.2% by incorporating 10 wt% DPA. The LOI of PBT increased at a certain extent for composites containing only ZnB. The LOI value of sample containing 30 wt% ZnB was 23.8%. The flame propagation rate was decreased, the amount of char residue was increased and less amount of smoke was produced with the increasing concentration of ZnB as observed during the tests. The LOI increased as the concentration of ZnB decreased for the samples containing ZnB and DPA. However, the measured values of LOI were above 25% for samples containing 5 wt% and 7.5 wt% ZnB.

Table 4. LOI test results of the samples

	Reference PBT	Additive								
		DPA (%)			ZnB (%)			ZnB+DPA		
		10	20	30	10	20	30	U1	U2	U3
LOI (%)	21.0	29.2	32.6	34.0	22.5	23.0	23.8	24.5	25.0	26.5

3.3. TGA Test Results

Figure 5 shows the DTA and TG graphs of the ZnB and PBT blends. The TG thermogram demonstrate that the presence of ZnB reduce the decomposition temperature of the PBT and increase the char content. Second endothermic peak appeared due to evolution of hydrated water which evolves in the temperature range 385-395 °C. The DTA graphs showed that released boron oxide (B_2O_3) leading to formation of protective glassy layer between 350 °C and 500 °C. Similarly, endothermic peaks which contributed to char formation were observed in the DTA graph of DPA doped samples between 350 °C and 450 °C. Figure 6 shows the thermogravimetric analysis results of DPA and PBT blends. Increasing DPA content had caused increasing the residue slightly. Results showed that flame retardant additive decomposes to volatile phosphinic acid and zinc compound and phosphorus residue.

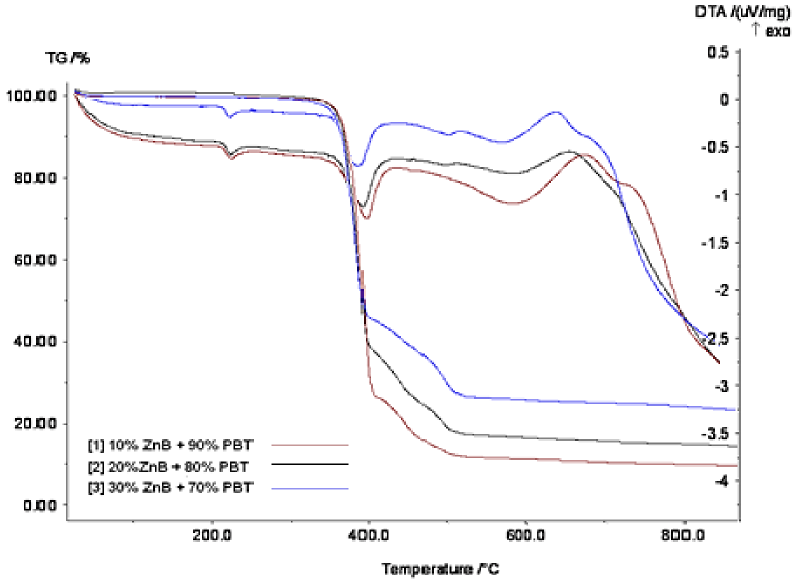

Figure 5. Thermal analysis test results of ZnB/PBT samples

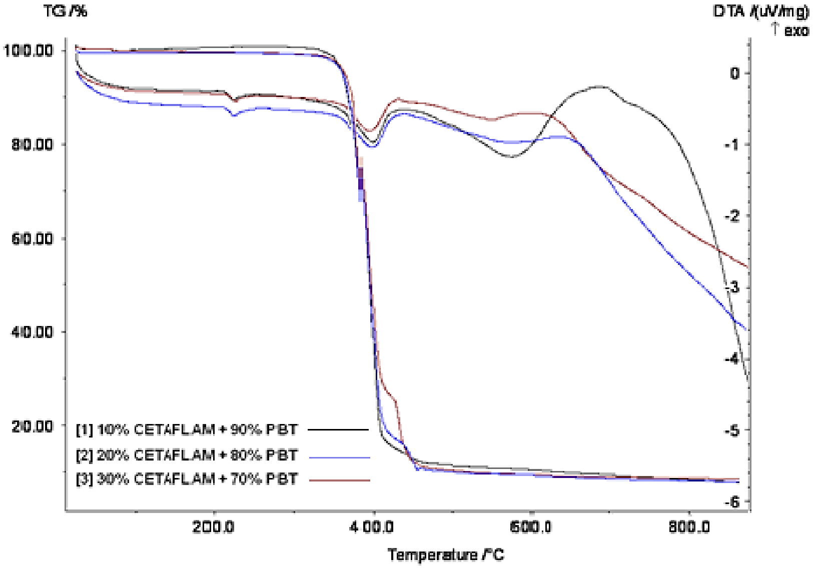

Figure 6. Thermal analysis test results of DPA/PBT samples

TGA and DSC curves and mass loss rate of samples containing DPA and ZnB are shown in Figure 7 and Figure 8 respectively. The temperatures at which 10 wt% and 50 wt% of the initial mass lost and the char yield by %wt at 500°C and 600°C for samples flame retarded with DPA and ZnB are given in Table 5. The thermograms of all samples were similar. One degradation step observed between 350 and 500 °C. On the other hand, onset temperature of weight loss and the char residue of the samples were different. $T_{10\%}$ values of three samples with different compositions were the same. 50% of the initial mass was lost at 392°C (U1 and U2) and 395 °C (U3). $T_{10\%}$ and $T_{50\%}$ values decreased with the increasing flame retardant additive content which implies that the additives decrease the initial degradation temperature and promote earlier charring. A notable flame retardant effect of zinc borate was observed between 400-500 °C. The residual char increased with the increasing ZnB concentration. The char residue of U1 sample was reached up to 16.82% at 500 °C.

PBT decomposed in a single step between 350 °C and 500 °C with a maximum of weight loss at 402 °C. When ZnB/DAP mixtures were added in PBT, the maximum of main weight loss was shifted to lower temperatures at 393 °C (Figure 9).

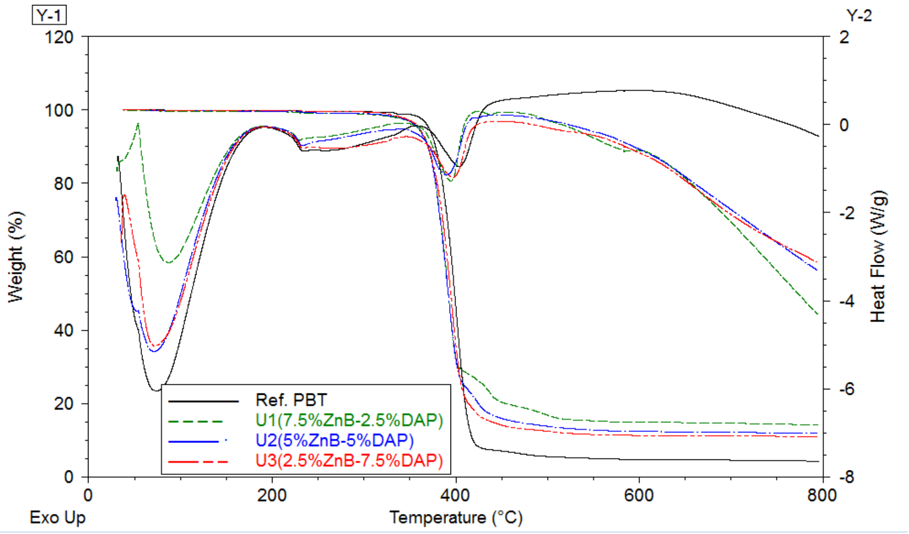

Figure 7. Thermal analysis test results of ZnB-DAP/PBT samples

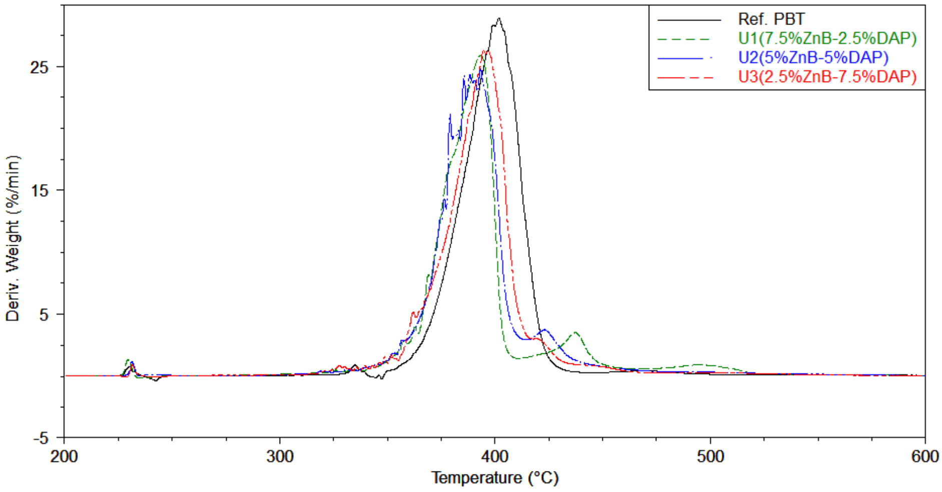

Figure 8. Mass loss rate of ZnB-DAP/PBT samples

Table 5. TGA results of DPA-ZnB/PBT samples

	$T_{10\%}$	$T_{50\%}$	**Char residue**	**Char residue**
			500 °C (%)	**600 °C (%)**
REF-PBT	378	399	5.57	4.73
U1	370	392	16.82	14.88
U2	370	392	13.79	12.37
U3	370	395	12.45	11.32

3.4. SEM Test Results

In order to investigate the dispersion of additives in polymer PBT samples containing 10wt% ZnB, 10wt% DPA and 5wt%ZnB-5wt% DPA were analyzed by scanning electron microscopy. The SEM images of these samples are shown in Figure 9.

Obviously, both phosphorus and zinc borate powders were homogenously distributed in the polymer. The particle sizes of the powders were in the range of 100-300nm. Zinc borate contributed to a non-homogenous distribution behaviour of powders. ZnB powders were caused roughness on the PBT surfaces.

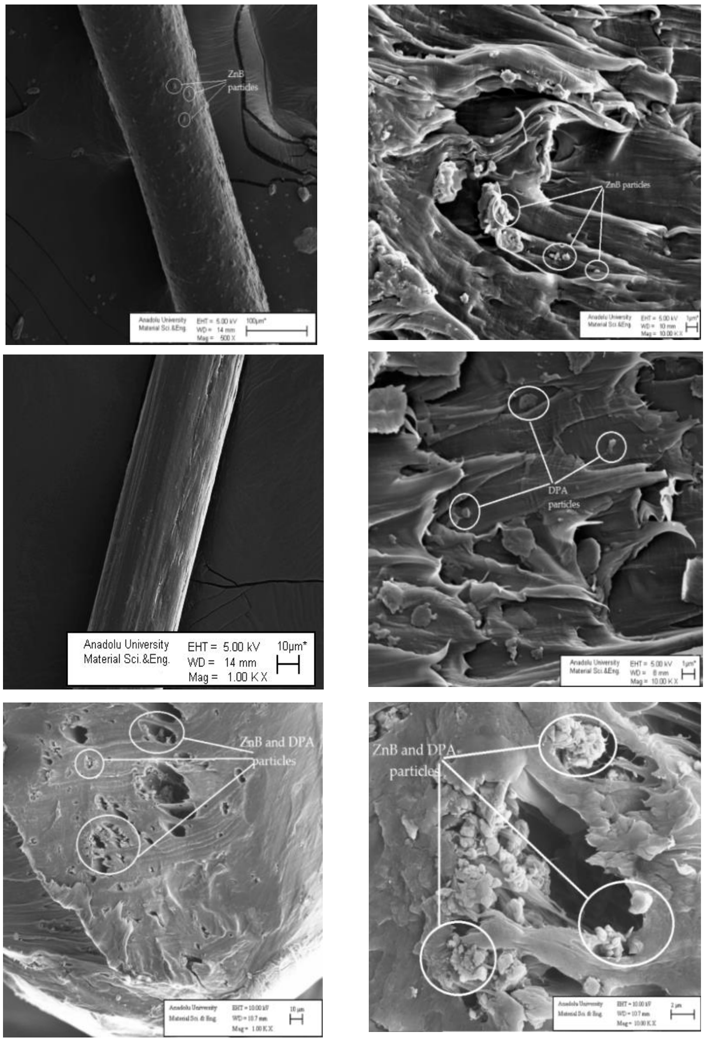

Figure 9. SEM images of samples with (a)10wt%ZnB, (b) 10wt% DPA, (c) 5wt% ZnB-5wt% DPA

4. CONCLUSIONS

The fire properties of the ZnB, organic phosphinate based flame retardant DPA and ZnB/DPA doped PBT were investigated and compared to each other by LOI and TGA tests. LOI values of ZnB/PBT samples are obtained very low even with higher filling content. This effect can be assigned to a filler effect (dilution of fuel) and to the formation of low viscosity glass protective coating due to decomposition of ZnB. Insulating layer formed on the surface of the PBT. It is attributed to the condensed phase activity of ZnB. At higher loading of ZnB, the dripping of the sample strongly decreased and char residue increased. It means that ZnB affect the mechanism of degradation of PBT and promote charring during the thermal degradation. The polymer decomposition was shifted to lower temperatures by ZnB. It was seen that organic diethyl phosphinic acid and zinc salt based additive DPA is particularly effective with PBT. Adding 10 wt% DPA increased the LOI to 29.2%. It is assumed that DAP released diethyl phosphinic acid in the gas phase during the main decomposition step. It is known that the diethyl phosphinic acid acts in the gas phase by inhibition of the combustion reactions.

It was concluded that the combination of DPA and ZnB can be used to increase the char residue and decrease the melt dripping of PBT. However, ZnB particles decreased the flame retardant efficiency (LOI value) of DPA.

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