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Aluminium trihydroxide in combination with ammonium polyphosphate as flame retardants for unsaturated polyester resin

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Abstract. The thermal and reaction to fire characteristics of a flame retardant unsaturated polyester (UP) ternary system are presented here. Thermal gravimetric analysis showed an improved thermal stability between 200–600°C with the addition of ammonium polyphosphate (APP) and aluminium trihydroxide (ATH) formulation. Cone calorimetry tests indicated that ATH is more efficient than calcium carbonate at delaying the ignition time, lowering the carbon monoxide yield and lowering the peak heat release (PHRR). However the addition of APP and ATH to the formulation failed to demonstrate any significant synergistic effect at reducing the PHRR.

Keywords: *thermosetting resins, unsaturated polyester, aluminium trihydroxide, ammonium polyphosphate, flame retardant*

1. Introduction

Unsaturated polyester resins (UP) are extremely versatile in terms of their properties and applications and have been a popular thermosetting resin for glass-fibre reinforced plastics (GRP) [1]. This matrix material has been used for many years in broad technology fields such as naval, offshore applications, automotive and construction industries. The reinforcement of polyesters has been traditionally with glass fibres. Recent studies replacing the traditional fibres with various cellulosic fibre reinforcements have shown promising results. These systems meet the environmental credentials without losing the characteristic properties of composite materials [2–4]. However despite the numerous advantages that polymeric materials provide to society in everyday life, there is an obvious disadvantage related to the high flammability of many polymers. Fire can be broken down into their constituent fire hazards: ignitability, ease of extinction, heat release rate, flame spread, smoke obstruction and smoke toxicity [5–7].

According to fire statistics, more than 12 million fires break out every year in the United States, Europe, Russia and China killing some 166 000 people and injuring several hundreds of thousands. Calculating the direct losses and costs for these countries is difficult, but $500 million per annum is an estimate based on some national data [8]. Therefore, in the pursuit of improved approaches to flame retardancy (FR) of polymers, a wide variety of concerns must be addressed. Competing with expensive flame retardant polymers as well as reducing the overall cost of the final product demands that the FR’s are kept at a reasonable cost. This limits the solutions to the problem primarily to

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additive type approaches. These additives must be easily processable with the polymer, must not excessively degrade the other performance properties, and must not create environmental problems in terms of recycling or disposal. Traditional systems such as brominated FR's (e.g. Hexabromocyclododecane (HBCD)) which has been used in many polymers including unsaturated polyester to prevent flame spread, but have significant disadvantages of producing dense smoke and corrosive combustion by-products which can have a negative impact on the environment. Another commonly used filler is alumina trihydrate or aluminium trihydroxide (ATH), which is looked upon as a 'greener' FR. The effectiveness of this flame retardant tends to be limited since relatively large amounts of the filler are needed for adequate flame retardancy (>60 wt%), which has a detrimental effect on the processing and as well as possible alterations to the mechanical properties of the final product. Some previous studies have shown improved flame retardancy of thermoplastic systems based on improving the effect of ATH in combination with other FR fillers such as nitrogen rich melamine [9]. Also, there has been some research carried out using combinations of aluminum trihydroxide together with ammonium polyphosphate (APP) in different polymer systems [10]. These studies resulted in some synergistic or antagonistic behaviour with respect to reducing the flammability of the polymer. To date, these two fillers have not been used together in a UP system. Therefore the purpose of this work is to carry out thermal and cone calorimetry studies on unsaturated polyester resin with ATH in combination with APP to create a flame retardant ternary system.

2. Materials and specimen preparation

This study consisted of bench scale fire testing a set of flame retardant unsaturated polyester specimens. The unsaturated polyester resin (UP) used was a P17 (ortho resin) from Reichhold Organic Chemicals Ltd. A non-flame retardant specimen consisting of 50 wt% calcium carbonate ($CaCO_3$) (~200 phr) supplied by Omya UK was prepared. The flame retardant fillers used were aluminum trihydroxide (OL104) from Albemarle Corporation and Exolit™ ammonium polyphosphate from Clariant. An unfilled unsaturated polyester specimen was also produced as a control specimen. To prepare the specimens, the fillers were dispersed in the UP under excessive shear mixing using a High Speed Mechanical Mixing (HSMM) Citenco, FHP Motors LC9 with four blades. The formulation was mixed for 5 min at 3000 rpm. The specimens were cured in an open steel mould with dimensions of 100×100 mm. The formulations (Table 1) were prepared and cured for 10 min at 140°C in an air circulated oven.

Table 1. UP formulations studied in this investigation

Specimens (weight percentage)
Unsaturated Polyester Resin (UP)
+50wt% Calcium Carbonate ($CaCO_3$)
+30wt% ATH
+40wt% ATH
+50wt% ATH
+50wt% ATH+5wt% APP
+50wt% ATH+10wt% APP
+50wt% ATH+15wt% APP

3. Experimental procedures

3.1. Cone calorimetry

All the tests for this study were conducted in the horizontal orientation. An irradiance of 50 kW/m^2 was used. Ignition was spark induced; specimens were run without a retainer frame and in triplicate and averaged.

3.2. Thermal analysis

Thermogravimetric analysis (TGA) was carried out using TA Instruments Q500 TGA at a heating rate of 10°C/min under air and nitrogen rich atmospheres; with a gas flow rate of 20 ml/min. In each case, specimens of approximately 5 mg were positioned in a platinum pan. Differential scanning calorimetry (DSC) analysis was carried out using Mettler Toledo DSC822e and closed aluminum pans with a pierced hole in the cover. Thermal scans were run from 30–350°C at 10°C/min with specimen masses averaging 5 mg, in air.

4. Results and discussion

4.1. Cone calorimetry

Inorganic hydroxide flame retardant additives decompose when heated, releasing water in the vapour phase of combustion (pyrolysis stage). As

Table 2. The delay in the time to ignition (TTI) for the FR UP specimens

Specimens	TTI [s]
UP	7
+50wt% $CaCO_3$	8
+30wt% ATH	20
+40wt% ATH	22
+50wt% ATH	24
+50wt% ATH+5wt% APP	26
+50wt% ATH+10wt% APP	27
+50wt% ATH+15wt% APP	30

this elimination of water results in an endothermic reaction, heat is removed from the substrate. This removal of heat slows down the decomposition of the substrate, which is indicated by the delay in time to ignition (TTI) (Table 2) and also the reduction in heat release rate (Figure 1).

This phenomenon allows the substrate to remain below its ignition temperature for the duration of the hydroxide decomposition process. Literature reports that the largest of the commercially used inorganic hydroxides absorbs between 1000 and 1500 J/g of energy during decomposition [11]. Although other references may cite different values for this parameter, the apparent discrepancies should not be of great concern, as they are relative. The values obtained depend on the type of equipment used to measure the endothermic response, the heating rate used, the sample size, particle size, crystal morphology, the method of sample preparation and the temperature range used in the determination. The addition of the fillers within the UP shows a delay in ignition times. Interference of the flame is due to the decomposition mechanisms of the individual fillers which are shown by the TGA and DSC thermograms, which will be discussed later. Cone calorimeter tests have been performed to estimate the reaction to fire of the flame retardant UP systems. Many reactions to fire parameters were determined, such as the time to ignition, the heat release rate, mass loss behaviour and the smoke production over time. In this study, tests were carried out at 50 kW/m^2 heat flux, which in the cone calorimeter is considered to represent a well developed fire [12]. The time to ignition data for the tested UP formulations is shown in Table 2. A marked improvement can be seen in the ATH filled formulations compared to unfilled ones with respect to delaying the ignition time. The UP had a TTI of 7 seconds and combusted violently with a large flame during testing. As the loading of ATH increases the TTI was prolonged.

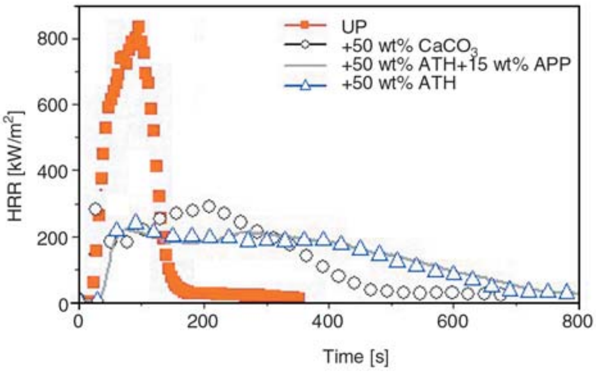

Figure 1. The reduction in heat release rate profile for the FR UP specimens

The ATH starts to break down in the temperature range of 180–200°C, conversion to aluminium oxide taking place in an endothermic reaction with release of water vapour. As a result of the endothermic breakdown, the UP is cooled, and thus fewer pyrolysis products are formed. The water vapour liberated has a diluting effect in the gas phase and forms an oxygen displacing protecting layer over the condensed phase [13].

Table 3 reports a PHRR of 836 kW/m^2 for the unfilled UP. This was reduced to 289 kW/m^2 with the introduction of $CaCO_3$, which is thought to occur for two reason; (i) more of the UP volume had been replaced by the filler, thus simply reducing the amount of combustible material present and (ii) when $CaCO_3$ decomposes it releases CO_2 which is thought to form around the flame front and thus diluting the combustion mixture [14].

As the ATH loading increased from 30 to 50 wt% the PHRR decreased from 337 to 244 kW/m^2, respectively. Inorganic hydroxides are generally used at levels of 50 wt% or more to attain the flame retardant results required. In this study 50 wt% was the maximum loading that could be achieved due to

Table 3. The peak heat release rate (PHRR) and total heat release (THR) of the FR UP specimens

Specimens	PHRR [kW/m^2]	THR [MJ/m^2]
UP	836	080
+50wt% CaCO3	289	85
+30wt% ATH	337	116
+40wt% ATH	319	113
+50wt% ATH	244	107
+50wt% ATH+5wt% APP	240	105
+50wt% ATH+10wt% APP	230	93
+50wt%ATH+15wt% APP	221	90

very high shear forces needed to disperse the highly viscous mixture. The results show that the calcium carbonate had a positive effect in reducing the PHRR. This was thought to be due to fuel replacement. The ATH reduced the PHRR further, the endothermic and water liberating effect reduced the combustion of the specimen. This was evident from PHRR for 50 wt% ATH and 50 wt% $CaCO_3$ loaded UP specimens, which were 224 and 289 kW/m^2 respectively. The addition of APP also reduced the PHRR. A formulation with the maximum ATH loading of 50 wt% was chosen to formulate three specimens with 5, 10 and 15 wt% APP, the PHRR were 240, 230 and 221 kW/m^2, respectively. Again the explanation for this reduction could be due to more inorganic filler being introduced into the resin thus less UP being available for combustion. However research by Levchik *et al.* [15] and Shen *et al.* [16] have shown a reaction between ATH and APP. Ammonium polyphosphate, a well known component of intumescent flame retardants is considered a shield coating precursor because of the formation of a continuous cross linked vitreous phase called ultraphosphate during thermal decomposition [17]. Whereas aluminium trihydroxide on thermal decomposition undergoes endothermic dehydration releasing water to the gas phase with the *in situ* formation of a thermally stable ceramic material alumina (Al_2O_3).

The formation of an Al_2O_3 surface layer acts in a similar way to an intumescent flame retardant whereby it shields the heat and mass transfer between the unsaturated polyester and the flame. The flame retardant effectiveness of ATH is however detrimental to the mechanical properties (not tested here), i.e. high loadings generally $\geq$ 50 wt% are necessary to reach a suitable flame retardant effect but results in a dense and brittle material [18, 19]. The combined use of ATH and APP was studied aiming at a more thermally stable P–Al–O surface coating instead of the P–O, bringing together film forming action of ultraphosphate with thermal stability of Al_2O_3 to improve high temperature surface protection of the polymer. Table 3 shows the total heat release (THR). Unfilled UP had a THR of 80 MJ/m^2, which increased for the specimen with the addition of ATH and APP. The total heat release is calculated by integrating the area underneath the HRR vs. Time curve. Due to the FR's prolonging the burn time for the specimens results in the slight increase in THR. Zhang *et al.* [20] proposed a correction factor based on theoretical analysis of taking account of the effective heat of combustion of the filler and polymer separately then multiple it with the individual mass loss rates. They suggested that if this correction factor was taken into consideration in their study, then the THR for a PP specimen loaded with 70 wt. % ATH would have been 6.5% lower. Nevertheless the most significant predictor of fire hazard is the heat release rate; therefore the rate at which heat is released is of more interest than the total amount [21, 22]. An increasing burn time is indicative of the FR additive impeding or hindering the combustion process. Also in general the most important factor in evaluating a material is the peak heat release rate (PHRR) as this signifies the time at which the material evolves the maximum amount of heat into the surrounding, this can give a crude indication of the time available to escape the fire before flashover (the near simultaneous ignition of all combustible material in an enclosed area). The unfilled UP reaches its PHRR of 836 kW/m^2 in 96 seconds and the 50 wt% ATH+15 wt% APP system reached its PHRR in 76 seconds but this was only 221 kW/m^2 which is almost 4 times lower than the unfilled UP.

Table 4 shows the time to peak effective heat of combustion (EHC) and average EHC for the specimens tested. The EHC is calculated from the THR and total mass loss, which was reduced from an overall average of 20.79 to 18.81 MJ/kg for the unfilled UP and 50 wt% ATH+15 wt% APP system, respectively. This is an indication of the combustion mechanism being interfered with, most likely in the vapour phase by the FR mechanisms of the aluminum trihydroxide and ammonium poly-

Table 4. The delay in time to peak effective heat of combustion (EHC) and the reduction in average EHC of the FR UP specimens

Specimens	**Time to peak EHC [s]**	**Average EHC [MJ/kg]**
UP	236	20.79
+50wt% $CaCO_3$	470	20.86
+30wt% ATH	600	19.92
+40wt% ATH	639	19.44
+50wt% ATH	652	19.28
+50wt% ATH+5 wt% APP	672	19.08
+50wt% ATH+10 wt% APP	728	18.91
+50wt%ATH+15 wt%APP	874	18.81

Table 5. The delay in the time to peak specific extinction area (SEA) for the FR UP specimens

Specimens	Time to peak SEA [s]
UP	136
+50wt% $CaCO_3$	420
+30wt% ATH	645
+40wt% ATH	668
+50wt% ATH	680
+50wt% ATH+5wt% APP	712
+50wt% ATH+10wt% APP	720
+50wt% ATH+15wt% APP	730

phosphate. Also, the time to peak EHC was delayed, which shows that the combustion is being hindered by the flame retardant mechanisms. The results of the smoke parameter measurements made in the cone calorimeter can be expressed in a number of different forms. Table 5 displays the time to peak specific extinction area (SEA), which is the total obstruction area of smoke produced, divided by the total mass loss during the burn.

The shift in the time to peak is most likely to be due to the FR formulations generating a protective charred layer which prevents volatiles and smoke evolving from the specimen's surface. Another important smoke measurement is the average smoke production release (SPR). The SPR is the area of obscuration produced per second. Figure 2 illustrates the effect of FR fillers on reducing the average SPR from 0.06 to 0.04 m²/s for the unfilled UP and 50 wt% ATH+15 wt% APP specimens, respectively. Table 6 lists the total smoke release (TSR) and total smoke production (TSP). The rise in these two properties is indicative of incomplete combustion. This smouldering (flameless combustion) effect results in a longer burn time which, allows for more smoke and soot debris to accumulate which is especially important here due to the high degree of aromatic content (especially the styrene) in the unsaturated polyester resin [23].

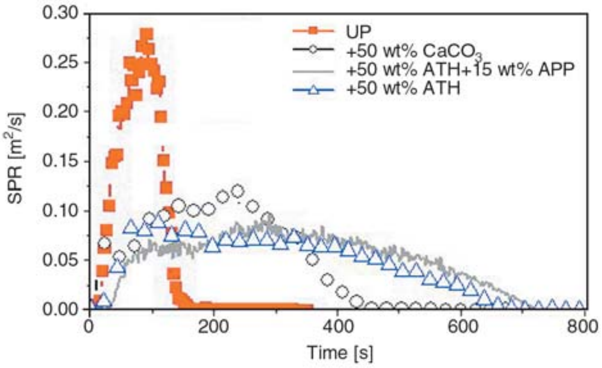

Figure 2. The effect on the smoke production release (SPR) of the FR UP specimens

The gas products released by a decomposing polymer substrate depend on the chemical nature of the organic constituents, oxygen availability, and temperature of the fire. Table 6 also displays the mean carbon monoxide yield (COY) in kg/kg. The mean COY is seen to be inversely proportional to the TSR and TSP. The theory behind this is that more carbon monoxide is liberated at a higher decomposition temperature in the UP. Cunliffe *et al.* [24] carried out this work on the pyrolysis behaviour of various polymers including unsaturated polyester. The generation of carbon oxides would be expected from the breakdown of ester bonds within the resin. The higher pyrolysis temperatures caused by the higher PHRR of the UP would result in more carbon monoxide to be evolved due to further cracking of the polyester chains. While the types and amounts can vary between materials, all polymers release carbon monoxide and carbon dioxide [25, 26]. Carbon monoxide is a major safety concern because it is lethal at a relatively low concentration, with human death occurring within one hour at a concentration of about 1500 ppm.

4.2. Thermal analysis

To examine the effect of FR's on the thermal stability and the decomposition behaviour, TGA data under nitrogen and air atmospheres were determined and analysed. The TGA curve of aluminum

Table 6. The total smoke release (TSR) total smoke production (TSP) and carbon monoxide yield (COY) measurements

Specimens	TSR [m²/m²]	TSP [m²]	Mean COY [kg/kg]
UP	2172	21.7	0.0311
+50wt% $CaCO_3$	3209	32.1	0.0243
+30wt% ATH	3442	34.4	0.0237
+40wt% ATH	3546	35.5	0.0232
+50wt% ATH	3811	38.1	0.0216
+50wt% ATH+5wt% APP	3838	38.4	0.0215
+50wt% ATH+10wt% APP	3914	39.1	0.0213
+50wt% ATH+15wt% APP	3996	39.5	0.0212

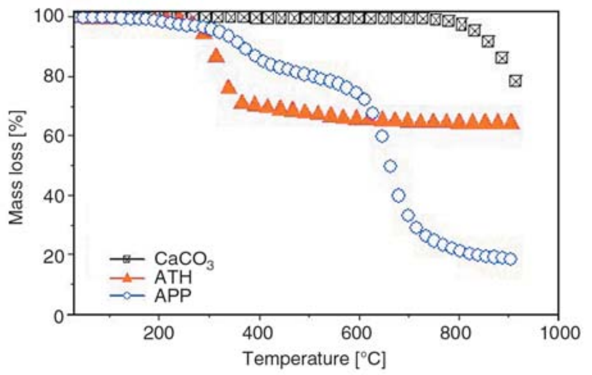

Figure 3. The TGA thermogram of fillers used in the UP formulations

trihydroxide (ATH) (Figure 3) which was heated to 900°C shows one main weight loss step at about 240°C which is due to endothermic release of its 35% water of crystallisation into the gas phase, this leads to the *in situ* formation of a ceramic layer of γ-Al_2O_3. Both the endothermic dehydration and the formation of the ceramic layer are responsible for the FR mechanism of inorganic hydroxides [27].

The TGA analysis carried out on ammonium polyphosphate (APP) shows that the elimination of ammonia and water starts at 190°C (maximum rate of weight loss at 370°C) with transformation of linear crystalline APP into a vitreous crosslinked ultraphosphate) which undergoes fragmentation to volatile P_2O_5. Ammonia evolution from APP is related to acidic sites formation involved in the intumescence phenomenon. Calcium carbonate ($CaCO_3$) thermally decomposes at a much higher temperature than the other two fillers. The single decomposition step occurred at 800°C which indicates a higher thermal stability. Calcium carbonate does not combust; it thermally decomposes and converts through the following mechanism; $CaCO_3 \rightarrow CaO + CO_2$. When $CaCO_3$ is heated to 800°C it liberates CO_2 and will thus become CaO. Figure 4a and 4b show the results of the UP formulations test in the TGA under air and nitrogen respectively. The formulations started to decompose at around 250°C due to the decomposition of the resin system. The unsaturated polyester started to decompose at 250°C, whereas the main weight loss occurred between 300 and 400°C. During thermal decomposition, it is thought that the polystyrene cross-links started to decompose first which was followed by volatilisation of the styrene. The linear polyester portion undergoes scission. Ferreira *et al*. [28] have shown that during thermal decomposition, volatiles are lost UP to 400°C while above 400°C; it is solid phase oxidation reactions that predominate. The 50 wt% $CaCO_3$ specimen demonstrated the best performance in terms of thermal stability when tested in air.

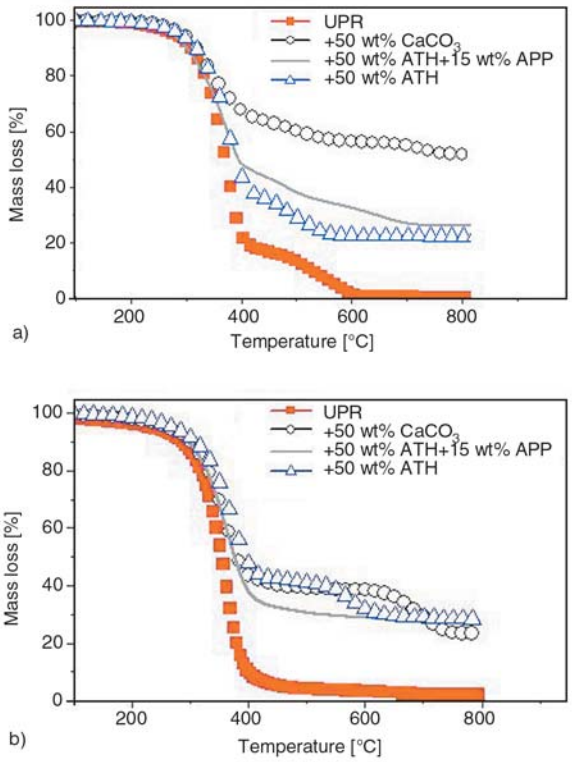

Figure 4. a) The effect of the various fillers and their combination on improving the thermal stability and residual mass of UP, b) The effect of the various fillers and their combination on improving the thermal stability and residual mass of UP tested in nitrogen

The ATH loaded specimens showed a marked improvement in residual weight retention at temperatures above 600°C as the loading level increase. This is thought to be due to the conversion of $Al(OH)_3$ to Al_2O_3 which is a thermally stable engineering ceramic which possesses a melting temperature of 2054°C. The addition of APP to the formulation also increased the residual mass, which was also observed for the cone calorimeter specimens (Table 7). It has been well documented that as APP decomposes it dehydrates and converts into an intumescent char; this could be the reason for the extra residual mass. The ATH+APP specimens which were run under nitrogen (Figure 4b) showed no major differences to those which were tested in air. Since the pyrolysis of polymers during fires are characterised by anaerobe decomposition, it was important to conduct the TGA tests in nitrogen as

Table 7. The peak mass loss rate, residual mass and average specific mass loss for the FR UP specimens from the cone calorimeter

Specimens	Peak mass loss rate [g/s]	Residual mass [%]	Average specific mass loss [g/s·m^2]
UP	0.420	6.8	34.4
+50wt% $CaCO_3$	0.220	36.7	11.1
+30wt% ATH	0.210	17.7	14.4
+40wt% ATH	0.170	18.7	13.7
+50wt% ATH	0.165	25.1	10.9
+50wt% ATH+5wt% APP	0.164	26.7	9.7
+50wt% ATH+10wt% APP	0.162	28.4	9.3
+50wt% ATH+15wt% APP	0.161	28.8	9.3

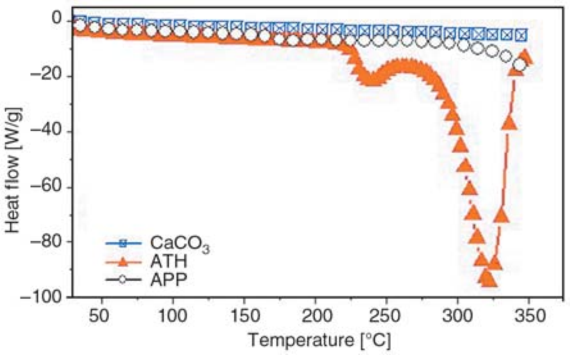

Figure 5. DSC thermogram of the unfilled fillers on their own

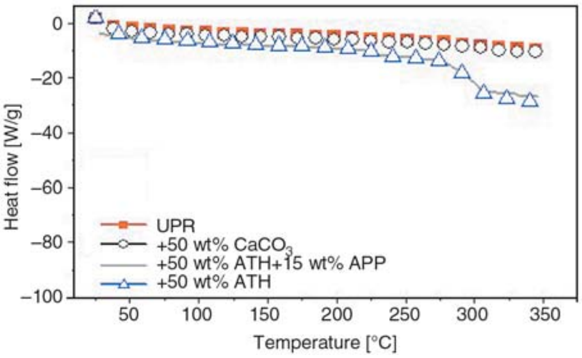

Figure 6. DSC thermogram of the FR UP formulations

well as thermo-oxidative conditions. With respect to char yields, the pure UP comprised of slight more at the end of the run. However the most significant difference was with the $CaCO_3$ specimen. There was rapid decomposition after 400°C and had only a 22% char yield whereas when tested in air it held stable up to 800°C in which it ended with a 55% char yield. The specimen not being able to form a protective skin in the presence of a nitrogen rich atmosphere was thought to be attributed to this difference [29]. Figure 5 shows the energy absorption profile investigated by differential scanning calorimetry (DSC) on the fillers. The aluminum trihydroxide absorbed the most significant amount of thermal energy out of all the fillers. The ATH underwent endothermic decomposition and absorbed 978 J/g of thermal energy. However, the other two fillers did not show any significant endothermic effects. The DSC scan of APP showed an endothermic process between 240 and 260°C which corresponds to polymorphic transitions of residual APP crystal structure form APP I to APP form II, above which ammonia and water elimination begins at low rates as seen from TGA (Figure 6).

This process decreases the concentration of fuel available for combustion and limits the amount of heat being fed back into the surrounding polymer. The result is a decrease in the mass burning rate for the polymer. Figure 6 shows the heat sink effect caused upon by the introduction of ATH into the UP resin. The direct result of this and the evolution of water vapour can be witnessed in Table 2 which shows TTI data. As the ATH loading increases so too does the time to combustion.

5. Conclusions

The purpose of this study was to observe any possible flame retardant improvements to commercial unsaturated polyester using 'greener' non-toxic flame retardants. The use of ATH in combination with APP was expected to impart an improved flame retardant effect in the UP system. A combination of both FR's showed an improved ignition delay time as well as decreases in the peak heat release rate and carbon monoxide yield. However, synergistic behaviour was not witnessed but instead a mere fuel replacement effect on the role of the fillers is more plausible. In general, synergism can be defined as two or more components working together to produce a result not obtainable by any of the components independently. The polymer used plays an important part in the effectiveness of these two FR fillers and their combination does not work with all polymers as shown in the literature. The additional reduction in the PHRR with the addition of APP does not justify its use due to the resultant difficulties with increased viscosity, which will result in major processing difficulties in adopting these materials in potential fibre reinforced composites.

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