“Thermal degradation behaviour of flame retardant unsaturated polyester resins incorporating functionalised nanoclays”, B K Kandola, S Gawande and A R Horrocks, in “Fire Retardancy of Polymers: New Applications of Mineral Fillers”, eds M Le Bras, C A Wilkie, S Bourbigot, S DuQuesne and C Jama, Royal Society of Chemistry, London, 2005, pp 147-159

Thermal degradation behaviour of flame - retardant unsaturated polyester resins incorporating functionalised nanoclays

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Abstract

This paper discusses the effect of nanoclays on thermal degradation of unsaturated polyester resin with and without conventional flame retardants. Unsaturated polyester nanocomposites were prepared by *in-situ* polymerization with exfoliated structures. Simultaneous DTA-TGA analysis showed that nanoclays reduce thermal stability of the unsaturated polyester resin below 600^{0}C and after that there was no change. Nanoclays also reduce the onset of degradation temperature of the resin. Above 600 ^{0}C, char formation is enhanced but not to the same extent as reported in literature for other polymer (e.g., nylon, polystyrene, etc.) – nanocomposite structures. The effect of conventional flame retardants - ammonium polyphosphate, melamine phosphate with and without dipentaeythritaol and alumina trihydrate on thermal degradation of resin was also studied. All these flame retardants enhance char formation of the resin above 400^{0}C and presence of nanoclays promotes further increase. Analysis of the thermogravimetric data indicates that this enhancement in char formation is not as much as expected when compared with similar other polymer - nanocomposite structures.

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Keywords: Unsaturated polyester; Nanocomposites, Flame retardants; Thermogravimetry

1. Introduction

The recent interest in the reported char - promoting behaviour of the functionalised dispersed nanoclays at levels of 2-5% to yield nanocomposite structures having improved fire properties, prompts their investigation as potential fire retardants [1-4]. The nanocomposite flame retardant mechanism is believed to be a consequence of high performance carbonaceous - silicate char build-up on the surface during burning [1]. This insulates the underlying material and slows down the mass loss rate of decomposition products. Unfortunately, however, these nanocomposites on their own are not sufficient to reduce flammability of low char-forming polymers like polyesters to a significant and specified level. However, when used with conventional flame retardants, their action may be synergistic in a way that less flame retardant is required as compared to the situation where nanoclays are not used. The other advantage is that nanoclays maintain and sometimes increase matrix mechanical properties while it is well known that any conventional additive in a polymer often reduces its mechanical performance [1-3,5].

To this effect we have explored the effect of incorporating different types of organically modified clays in polyester resin with and without flame retardants, such as ammonium polyphosphate, melamine phosphate with and without dipentaerythritol and alumina trihydrate. The clays have been introduced at 5% loading level under high shear. X-ray diffraction studies have shown that the clays are well exfoliated. Thermal degradation behaviour of these samples has been studied by simultaneous DTA-TGA and results have been analysed to assess possible effects of nanoclays on resin thermal stability with and without flame retardants.

2. Experimental

“Thermal degradation behaviour of flame retardant unsaturated polyester resins incorporating functionalised nanoclays”, B K Kandola, S Gawande and A R Horrocks, in “Fire Retardancy of Polymers: New Applications of Mineral Fillers”, eds M Le Bras, C A Wilkie, S Bourbigot, S DuQuesne and C Jama, Royal Society of Chemistry, London, 2005, pp 147-159

2.1. Materials

Resin : Polyester resin - Orthophthalic, Crystic 471 PALV (Scott Bader)

Clays : Cloisite Na^+, 10A, 15A, 25A and 30B (Southern clay Products, USA). Properties of these clays are given in Table 1.

Flame-retardants (FR) : The following commercially available flame retardants were used without further purification :

(i) APP - ammonoium polyphosphate (Antiblaze MCM, Rhodia Specialities)

(ii) NH - melamine phosphate (Antiblaze NH, Rhodia Specialities)

(iii) NW - dipentaerythritol / melamine phosphate (Antiblaze NW, Rhodia Specialities)

(iv) ATH - alumina trihydrate (Martinal, Martinswerk, GmbH)

2.2. Preparation of polyester-clay nanocomposites

The polyester-clay nanocomposites incorporating flame retardants have been prepared by in-situ intercalative polymerisation. 5%(w/w) clay was gradually added to the resin polyester resin, while stirring with a mechanical mixer under high shear (900 rpm). The mixing was carried out for 60 min at room temperature. For samples incorporating flame retardants, 20% (with respect to resin-clay mixture) of the respective flame retardant was added to the mixture of resin and clay after 20 min of mixing. The percentages of various components in the formulations are given in Table 2. Small amounts of samples were taken from the mixture for simultaneous DTA-TGA analysis before the catalyst was added and laminates were cast and cured at room temperature for further flammability testing (to be discussed in further publications).

The nanocomposite structures were characterised by X-ray diffraction, XRD, in the laboratories of the National Institute of Standards and Testing (NIST), USA.

2.3. **Equipment**

Thermal analysis : Simultaneous DTA-TGA analysis was performed using SDT 2960 TA instruments under flowing air (100 ml/min) and at a heating rate of 10K min^{-1} on 25 mg sample masses.

3. Results and discussion

The nanocomposite formation has been studied by X-ray diffraction measurements. In the diffraction curves for pure clays, a prominent peak in each curve corresponding to basal spacing of respective clays occur at d-spacings as shown in Table 1. This reflection is missing in the scattering curves of all the polyester-clay nanocomposites, irrespective of presence of flame retardant, confirming the presence of nanocomposite structures. While detailed XRD analysis will be presented in a separate publication, here represntative diffraction curves for polyester-Cloisite 25A with and without APP are given in Fig.1. Cloisite 25A shows a peak at 2θ of 4.8^0, represnting d-spacing of 18.6A^0 (see Table 1), which is missing in Res/Cl and Res/Cl/APP formulations in Fig.1.

3.1. Thermal degradation of clays

DTA and DTG peak maxima for all organically modified clays uesd in this work are given in Fig.2 and Table 3. Although Na-montmorillonite was not dispersed in polyester resin, its thermal analytical behaviour is discussed here for comparison with other organically modified clays. Na-montmorillonite shows very little weight loss as seen from Fig.2(a) and high char residues at 800 ^{0}C. In the main the DTA response is featureless (see Fig.2(b)) showing inertness of inorganic clay, however there are two very broad and small endotherms with maxima at 78 and 663^{0}C. All organically modified clays, however, show two stages of weight loss, the first represented by double peaked (in the temperature range of 235-293 and 307-348^{0}C) and the second by single peaked DTG maxima (575-605 ^{0}C) shown in Table 3. The first stages are most probably due to decomposition of respective organic components of the clays and the second single one due to dehydroxylation of the clay layers [6]. The residues at 800 ^{0}C in Table 3 represent the residual silica contents. These two stages of weight loss are also supported by DTA curves where all organically modified clays show double peaked exotherms. The first maxima occurs in the range 258 - 270 ^{0}C, and the second and more prominent around 345-355 ^{0}C.

3.2. Thermal degradation of resin

The TGA curve of polyester resin shows three stages of weight loss (see Fig.3(a)), the first occurring up to about 250 ^{0}C, the second over the range 250 - 400^{0}C and the third smaller weight loss from 400 to 600^{0}C. DTA (Fig.3(b)) and DTG peaks for polyester resin in Table 3 upto about 420 ^{0}C probably represent release of styrene and other volatile products. Resin starts to decompose above 250 ^{0}C, whereas the main step of weight loss occurs between 300 and 400 ^{0}C [7] as shown by the DTG peak at 360 ^{0}C in Table 3. Above 400 ^{0}C, solid phase oxidation reactions predominate [8]. The detailed mechanism of these reactions is discussed elsewhere [9].

3.3. Effect of different clays on thermal degradation of resin

One of the most important property enhancements expected from formation of a polymer nanocomposite is that of thermal stability either of the initial stages or final carbonaceous residues. However, for polyester nanocomposites, Figs.3(a) and (b) show that thermal stability of the resin is reduced below 400 ^{0}C. Furthermore, the main DTA decomposition peak of the resin at 313^{0}C is replaced by endotherms in Res/Cl nanocomposite samples. The initial endothermic DTA peaks (see

Table 3) in the 154-163 ^{0}C range are most probably due to decomposition of the organic component of the clay. The onset of degradation of resin temperature at about 250 ^{0}C is lowered on addition of nanoclays as reflected in shifts in DTG peaks from 313 ^{0}C to as low as 292 ^{0}C for the Res/Cl 4 combination as can be seen from Table 3 and Fig.3 (a). Similar effects of nanoclays in crosslinked polyester resin thermal analysis responses were also seen by Bhardwaj et al [10], where they introduced clay at 1, 2.5, 5 and 10% (wt/wt). Above 600 ^{0}C thermal stability is increased slightly as seen from Fig.3(a).

In Fig.3(c) are presented mass difference versus temperature plots, which show the difference between TGA experimental residual masses and calculated (from weighted avearge component responses) masses at each temperature [11]. Below 400 ^{0}C, char formation in all nanocomposites is much less and hence volatilization greater than expected, which may be because clays are interfering with the cross-linking of the resin. Between 400 - 600 ^{0}C again char formations are less than expected. Above 600 ^{0}C, char formations are similar to the expected from respectively calculated values. However, the type of clay has no effect on residual char formation at high temperatures. This gives clear indication that nanoclays on their own are not effective in increasing char formation and hence, reducing flammability of unsaturated polyester resins. However, Gilman et al have also observed this behaviour with vinyl ester and epoxy nanocomposites, where there is little improvement in carbonaceous char yield once the presence of silica is accounted for, but these samples showed reduction in peak heat release when tested with cone calorimetry [12].

3.4. Effect of flame retardants on thermal degradation of polyester resin

TGA curves of resin with all flame retardants are given in Fig.4(a); DTA and DTG peaks are given in Table 3. All flame retardants affect the thermal degradation mechanism of the resin. Thermal degradation mechanisms of ammonium polyphosphate, melamine phosphate with and without dipentaerythritol are discussed in our previous communications [13], where all of them show endothermic decomposition peaks. APP starts decomposing just after melting at 210 ^{0}C, releasing ammonia and phosphoric acid and then polymerises to polyphosphoric acid, which at higher temperatures decomposes to P_2O_5. These reactions are represented by an endothermic peak at 300 ^{0}C and exothermic peak at 668^{0}C, respectively (see Table 3). Melamine phosphate decomposes over the temperature range 250-380 ^{0}C, forming melamine pyrophosphate and polyphosphate at about 280 and 310 ^{0}C [13], decomposing further in the temperature range 330-410^{0}C releasing melamine, ammonia and water [14], shown by endothermic peaks at 270, 303 and 386^{0}C. In Antiblaze NW, dipentaeythritol melts at about 125^{0}C and reacts with melamine phosphate, forming polyol phospate. Antiblaze NH also shows a series of endothermic peaks at 118, 221, 241, 392^{0}C, followed by exothermic peaks at 492 and 665^{0}C. ATH decomposes between 180-340 ^{0}C with endothermic peaks at 95^{0}C and double peaked at 207 and 240, 299 and 348^{0}C (see Table 3), due to release of water and subsequent decomposition.

All of these flame retardants are therfore decomposing in the temperature range 200-300 ^{0}C, and so offer the chance of interacting with the cross-linking polyester resin. This is seen by changes in weight loss in this temperature range by TGA curves in Fig.4(a) and DTA peaks in Table 3. Ammonium polyphosphate enhances the thermal stability of resin, whereas, melamine phosphate with and without dipentaerythritol and alumina trihydrate, decrease its thermal stability, showing more weight loss in this temperature range. However, above 400^{0}C, all flame retardants enhance residual levels and hence thermal stability. APP is seen to be most effective char promoter upto 700^{0}C, after which the char oxidises. Alumina trihydrate shows superior behaviour above this latter temperature and even at 800 ^{0}C, 10% char is left behind (see Table 3), which is expected to be residual alumina. When the char difference between actual and calculated values are plotted in Fig.4(b), all the observations discussed above are clearly seen, except that APP is not producing more than expected char formation below 400 ^{0}C as previously observed in Fig.4(a). Moreover, ATH is not producing more than expected char above 700^{0}C, showing that this acts more as a filler rather than reactive flame retardant.

3.5. Effect of clays on thermal degradation of flame retarded resin

Although all the resin clay nanocomposites were studied with different flame retardants present, only results of Cloisite 25A (Cl 3) are presented here. From Fig.5(a) it can be seen that clay is effective in the case of the resin-APP mixture to change thermal degradation making it less stable than Res/Cl mixture at lower temperatures and producing more char above 500 ^{0}C as seen from Table 3 and as seen in the absence of nanoclay in Fig.4(a). Clay addition has less effect on resin containing melamine phosphate with and without dipentaerythtritol and alumina trihydrate as can be seen by comparing Figs.4(a) and 5(a). This effect can also be seen in Fig.5(b), where differntial curves are very similar in the range 100 - 400 ^{0}C. Clearly clay with ammonium polyphosphate is the most effective of samples studied to enhance char formation, yielding above 10% at 700 ^{0}C. However, this enhanced char is less than that seen for APP alone in Fig.4(b). This is in contrast to what is expected from such structures for other polymer - nanocomposites [2].

In Fig.6 the effect of clay on the Res/FR systems is shown by substracting Res/FR char difference values (Fig.4(b)) from Res/Cl 3/FR (Fig.5(b)). It can be seen that clay reduces char formation tendency of Res/APP system upto 700 ^{0}C and then it is increased up to 5%. In the presence of melamine phosphate clay further increases char between 450 - 700 ^{0}C. However, when both mealmine phosphate and dipentaerythritol are present, char formation tendency is reduced and similarly clay addition reduces the charring tendency of resin in presence of ATH.

The majority of the work in the area of polymer nanocomposite flame retardancy has been in thermoplastics, where it is proposed that reduction in heat release (flammability) and hence, increase in thermal stability is due to formation of a protective surface barrier / insulation layer consisting of accumulated silica platelets with a small amount of carbonaceous char [15, 16]. The accumulation or precipitation of silicate layers on the surface is due to gradual degradation and gasification of the polymer. However, according to Lewin [17] the layered silicates are dispersed and not dissolved in the polymer and should not precipitate as a consequence of the progressive gasification of the polymer. Lewin has postulated that this migration is driven by the lower surface free energy of the montmorillonite and by convection forces, arising from the temperature gradients, perhaps aided by movement of gas bubbles present during melting of the thermoplastic polymers. Alternative or even additional mechanisms include their presence as dispersed barriers to diffusion of molten polymer and decomposing products including release of combustible gases as well as diffusion of air and heat by convection. Each of these permeabilities contributes to the FR effectivity of the charred surface [17]. Clearly such complex mechanisms could interact positively or negatively with flame retardants also present and the evidence above suggests that both possibilities exist with the polyester resin used.

4. Conclusions

In unsaturated polyester resin nanocomposites, nanoclays reduce thermal stability and char formation tendency of the resin upto 600 ^{0}C and after that there is no observed change. Different condensed phase active flame retardants increase char formation of the resin above 400 ^{0}C. When nanoclays are added char formation is not greatly affected and in fact for APP - containing resins, reduced. Clearly for unsaturated polyester resin some char consolidating agent/group is required and work is ongoing in this area in our laboratories. However, thermal analysis techniques are not representative of the real fire situation. Consequently, the effect of these nanoclays on the resin fire performance with and without flame retardants in cone calorimetry will be presented in a separate publication, where their mechanical properties will also be evaluated.

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Captions

Fig 1. XRD data for unsaturated polyester with Cloisite 25 A (Cl 3) clay with and without APP.

Fig.2. a) TGA and b) DTA responses for all clays in air.

Fig.3. a) TGA and b) DTA responses in air ; c) percentage residual mass differences (actual - calculated) as function of temperature for different resin - clay nanocomposites.

Fig.4. a) TGA responses in air and b) percentage residual mass differences (actual-calculated) as function of temperature for resin with different flame retardants.

Fig.5. a) TGA responses in air and b) percentage residual mass differences (actual-calculated) as function of temperature for resin nanocomposite with different flame retardants.

Fig.6. Effect of Cloisite 25 A clay : percentage residual mass differences between Res/Cl 3/FR (Fig.5b) and Res/FR samples (Fig.4b).

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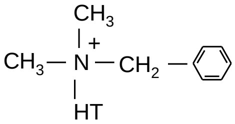
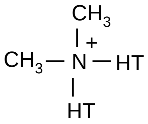
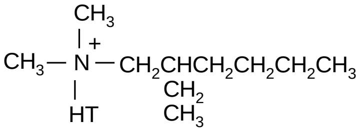
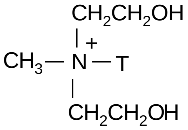
Table 1. Treatment/ properties of organically modified clays

Clay	Commercial name	Organic modifier*	Modifier conc. (meq/100g clay)	d spacing (Å)
Inorganic	Cloisite Na^+	-	93	11.7
Cl 1	Cloisite 10A		125	19.2
Cl 2	Cloisite 15A	 $CH_3-\overset{CH_3}{\underset{HT}{N^+}}-HT$	125	31.5
Cl 3	Cloisite 25A	 $CH_3-\overset{CH_3}{\underset{HT}{N^+}}-CH_2\underset{CH_2CH_3}{CH}CH_2CH_2CH_2CH_3$	95	18.6
Cl 4	Cloisite 30B	 $CH_3-\overset{CH_2CH_2OH}{\underset{CH_2CH_2OH}{N^+}}-T$	90	18.5

Note : * T is tallow and HT is hydrogenated tallow (~65%C18; ~30%C16; ~5%C14)
Anion : Chloride in Cloisite 10A, 15A and 30A ; sulphate in 25A

Table 2. Weight percentages of various components in the formulations

Sample		Resin (%)	FR (%)	Clay (%)
Res	- Resin	100	-	-
Res / Cl	- Resin + Clay	95	-	5
Res / FR	- Resin + FR	83	17	-
Res / Cl / FR	- Resin + Clay + FR	79	17	4

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Table 3. Analysis of DTA responses (peak temp ^{o}C), DTG maxima (^{o}C) and % mass residue of unsaturated polyester resin formulations under flowing air.

Sample description	DTA peaks (^{0}C)	DTG peaks (^{0}C)	% Mass residue	
			600 ^{o}C	800 ^{o}C
Clays				
Na^{+}	-	76, 665	91	88
Cl 1	347 Ex ; 633 Ex (s,b)	235, 348 ; 597	68	62
Cl 2	264 (s), 354 Ex(d); 545 Ex (s,b)	260, 307 ; 575	63	56
Cl 3	258 (s), 351 Ex (d); 626 Ex (s,b)	293, 341 ; 603	73	66
Cl 4	270 (s), 345 Ex (d); 630 Ex (s,b)	263, 335 ; 605	77	67
Resin	131 Ex(s,b) ; 313 (s), 365 Ex(d) ; 552 Ex	201, 360, 554	1.1	1
Resin /clays				
Res / Cl 1	163 En (s) ; 307 Ex ; 338 En ; 532 Ex	161, 338, 567	4	4
Res / Cl 2	158 En (s), 310 Ex ; 338 En ; 524 Ex	156, 337, 533	4	4
Res / Cl 3	159 En (s) ; 302 Ex ; 340 En ; 519 Ex	157, 338, 531	6	5
Res / Cl 4	154 En ; 292 Ex ; 333 En ; 528 Ex	147, 330, 533	6	5
Flame retardants				
APP	96 En (s); 173 En (s) ; 330 En ; 669 Ex	331, 655	62	8
NH	267 En ; 302 En ; 386 En ; Exo baseline deviation - 529, 756 (b)	267, 305,383, 472, 573, 740	41	18
NW	118 En (s) ; 221 En ; 241 En : 328 Ex ; 393 En ; 492 Ex ; 665 Ex	120, 238, 341, 389, 653	32	1
ATH	95 En ; 207, 240 En (d) ; 299, 348 En ; 422 Ex	191, 243, 307, 338, 727	47	38
Resin/FRs and/or clays				
Res / APP	320 En, 346 Ex (s), 382 Ex; 696Ex	317, 372, 699	30	3

Res / Cl 3 / APP	146 En (s) ; 290 Ex ; 313 En ; 351, 455, 530 Ex(t) ; 712 Ex(b)	155, 312, 745	23	15
Res / NH	266 En ; 297 Ex ; 313 En ; 323 Ex ;528 Ex ; 795 Ex ; 846 Ex	69, 306, 800	16	7
Res / Cl 3 / NH	174 En ; 257 En ; 312 En, 323 Ex ; 588 Ex	169, 310, 610	16	9
Res / NW	204 En ; 250 En ; 312 En ; 331 Ex ; 530 Ex ; 815 Ex	135, 311, 537, 801	16	7
Res Cl 3 / NW	155 En ; 251 En ; 306 En ; 329 Ex ; 458, 588 Ex (d)	151, 310, 613	15	7
Res / ATH	161 En ; 337 Ex ; 545 Ex	154, 314, 552	14	10
Res / Cl 3 / ATH	158 En (s); 186 Ex (s) ; 353 Ex ; 471 (s), 542 Ex (d)	153, 331, 566	14	11

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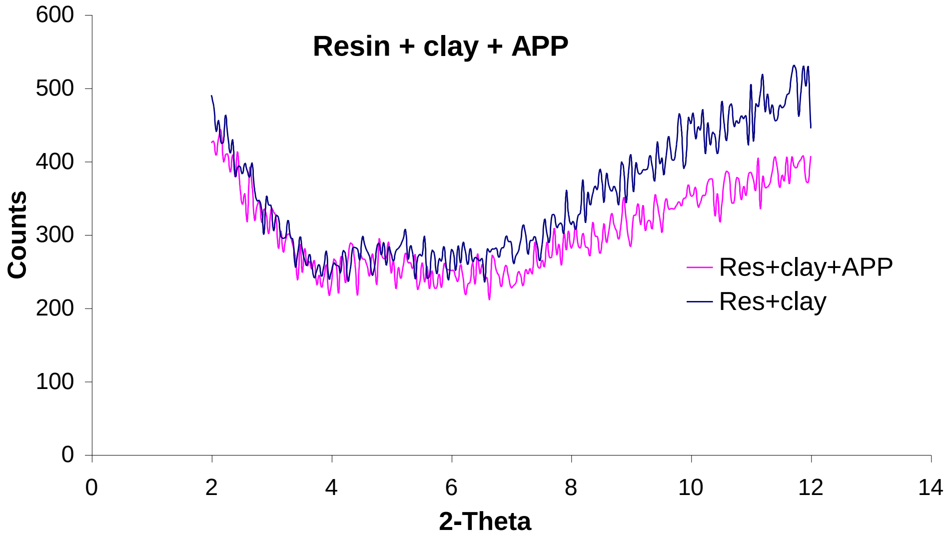


Fig 1. XRD data for unsaturated polyester with Cloisite 25 A (Cl 3) clay with and without APP.

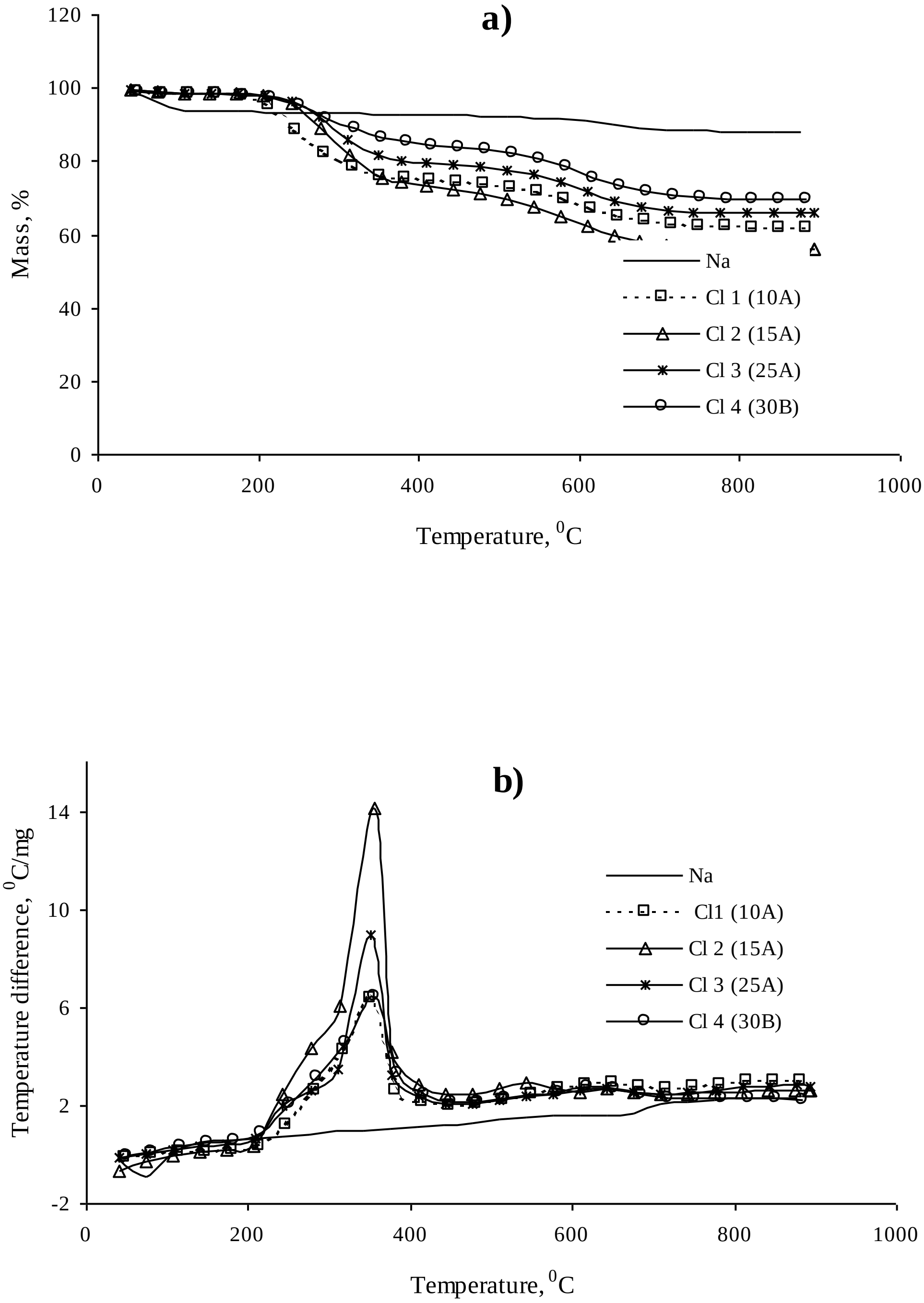
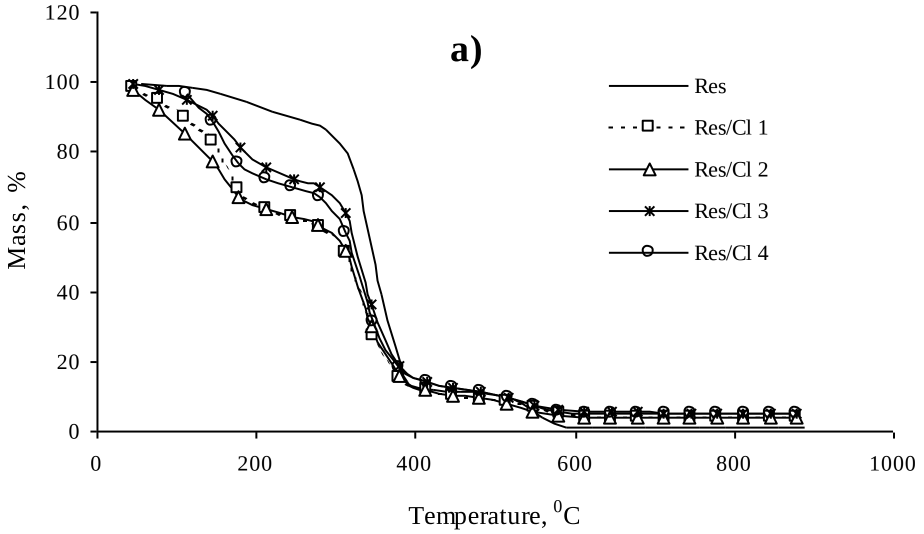
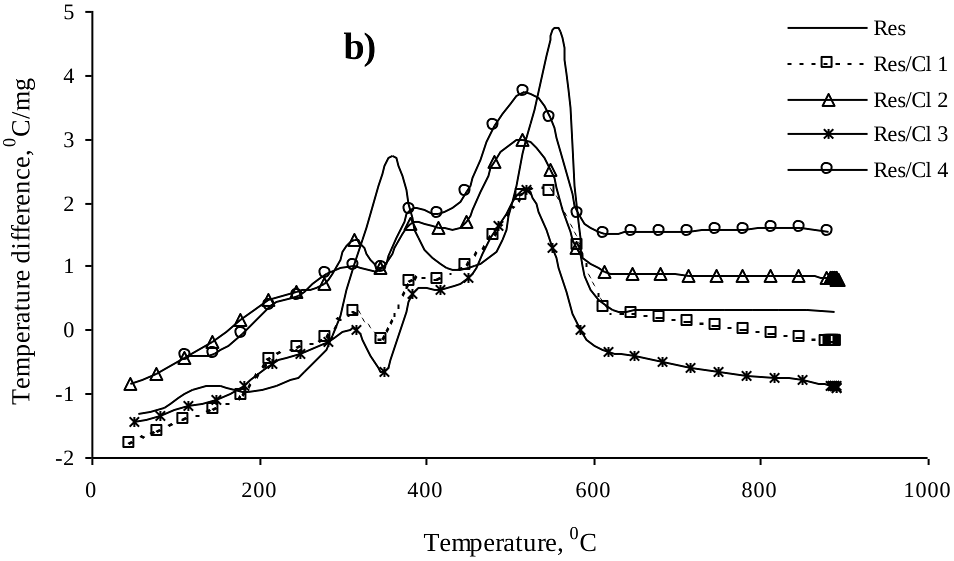


Fig.2. a) TGA and b) DTA responses for all clays in air.


a)
120
100
80
60
40
20
0
Mass, %
0
200
400
600
800
1000
Temperature, ^{0}C
Res
Res/Cl 1
Res/Cl 2
Res/Cl 3
Res/Cl 4


b)
5
4
3
2
1
0
-1
-2
Temperature difference, ^{0}C/mg
0
200
400
600
800
1000
Temperature, ^{0}C
Res
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Res/Cl 2
Res/Cl 3
Res/Cl 4

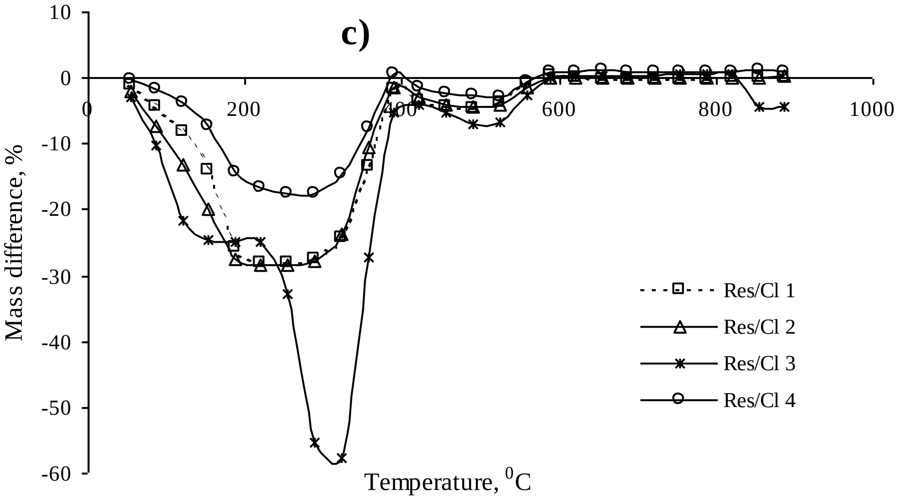
c)
10
0
-10
-20
-30
-40
-50
-60
Mass difference, %
0
200
400
600
800
1000
Temperature, ^{0}C
Res/Cl 1
Res/Cl 2
Res/Cl 3
Res/Cl 4

Fig.3. a) TGA and b) DTA responses in air ; c) percentage residual mass differences (actual - calculated) as function of temperature for different resin - clay nanocomposites.

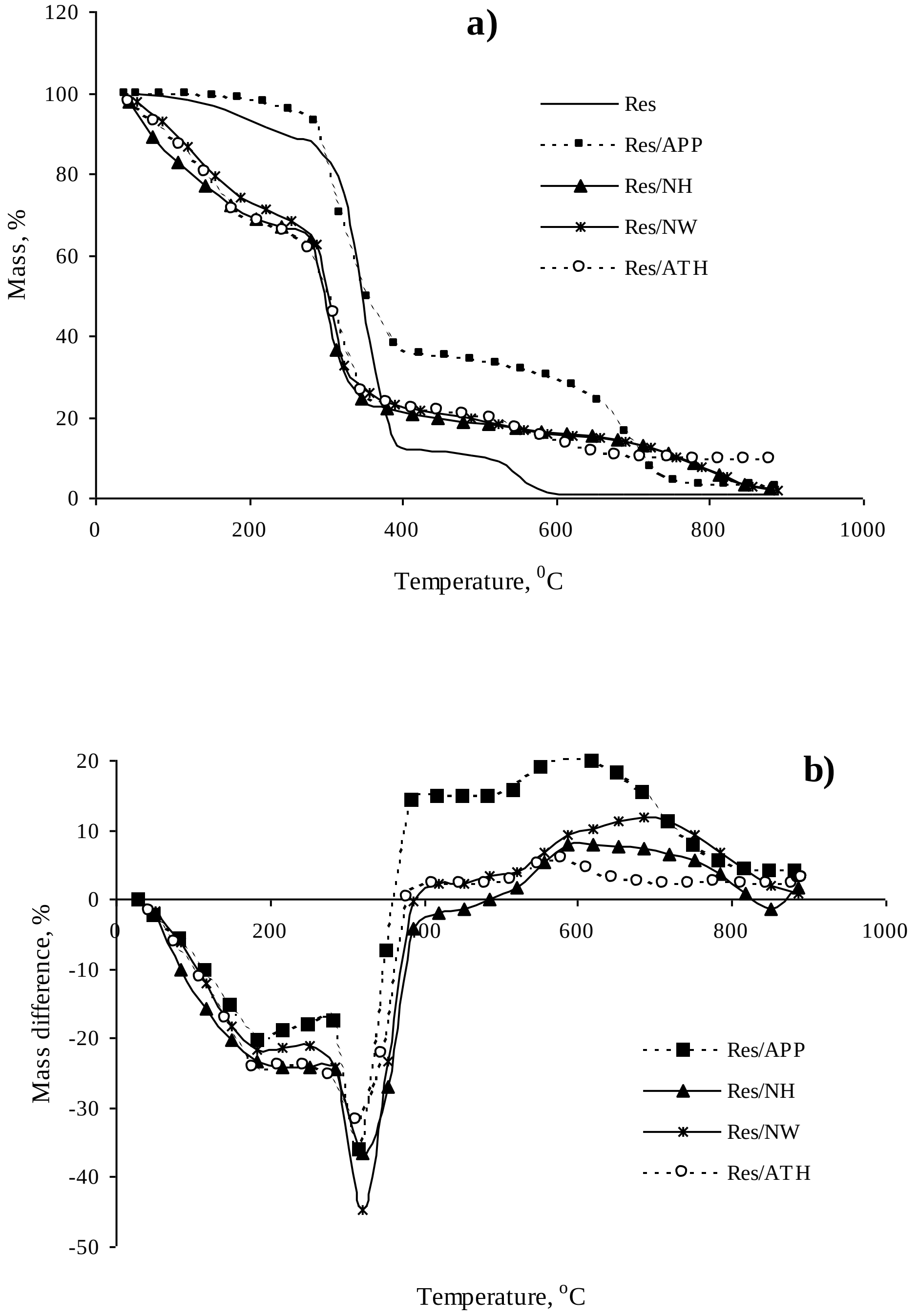

Fig.4. a) TGA responses in air and b) percentage residual mass differences (actual-calculated) as function of temperature for resin with different flame retardants.

“Thermal degradation behaviour of flame retardant unsaturated polyester resins incorporating functionalised nanoclays”, B K Kandola, S Gawande and A R Horrocks, in “Fire Retardancy of Polymers: New Applications of Mineral Fillers”, eds M Le Bras, C A Wilkie, S Bourbigot, S DuQuesne and C Jama, Royal Society of Chemistry, London, 2005, pp 147-159

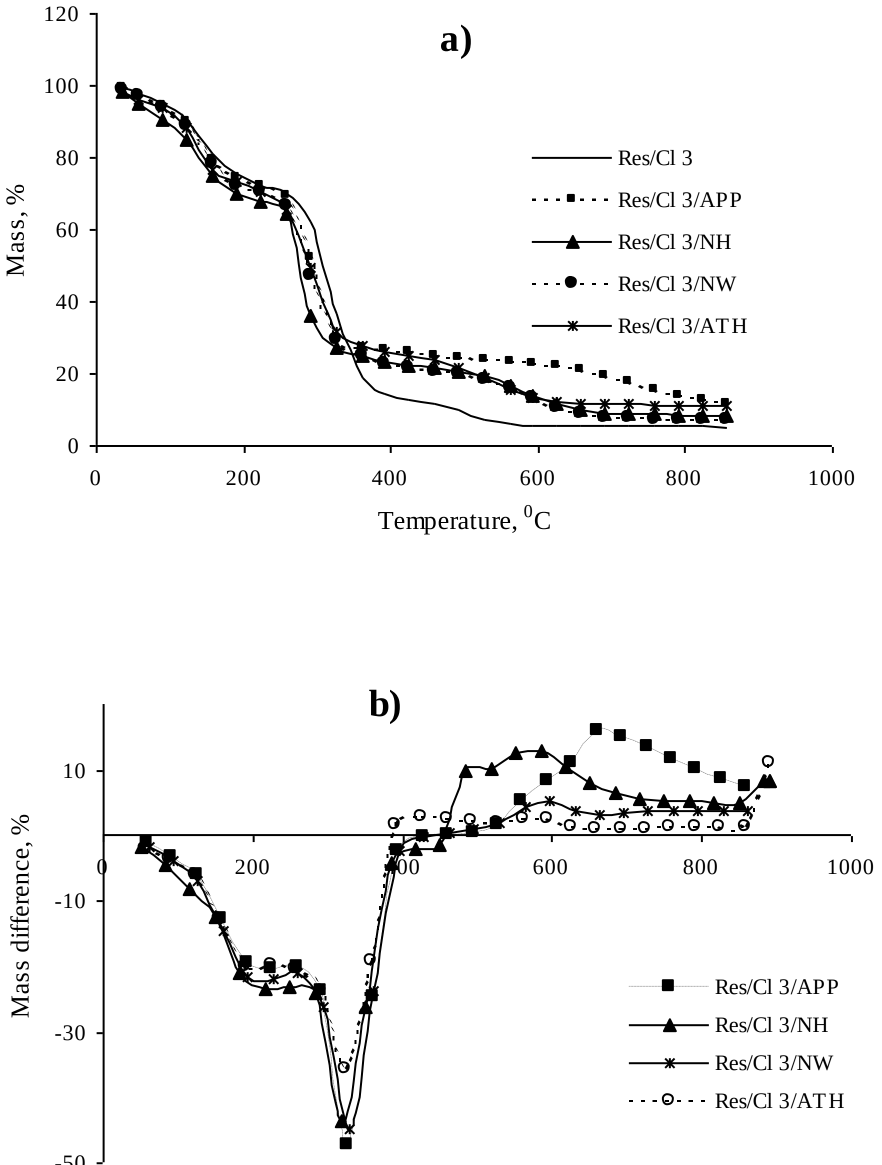

Fig.5. a) TGA responses in air and b) percentage residual mass differences (actual-calculated) as function of temperature for resin nanocomposite with different flame retardants.

“Thermal degradation behaviour of flame retardant unsaturated polyester resins incorporating functionalised nanoclays”, B K Kandola, S Gawande and A R Horrocks, in “Fire Retardancy of Polymers: New Applications of Mineral Fillers”, eds M Le Bras, C A Wilkie, S Bourbigot, S DuQuesne and C Jama, Royal Society of Chemistry, London, 2005, pp 147-159

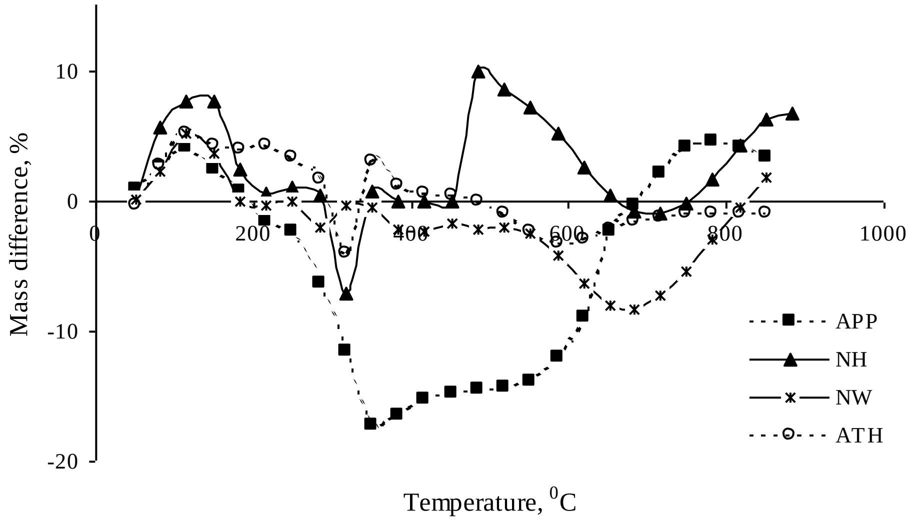

Fig.6. Effect of Cloisite 25 A clay : percentage residual mass differences between Res/Cl 3/FR (Fig.5b) and Res/FR samples (Fig.4b).