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Synthesis and use of hydrotalcites as heat stabilisers in thermally processed powdered polyvinylchloride (PVC)

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Lead-based stabilisers, such as lead sulphate and lead stearate, currently used in the processing of polyvinylchloride (PVC) products are being substituted with more environmentally safe, economically viable and higher quality materials. This study aimed to use hydrotalcites (HTs), which are environmentally non-hazardous and simple to synthesise, to effectively quench the HCl gas evolved during the degradation of PVC. From the results obtained in this study, the effects of varying the metal ion ratios in Mg/Zn/Al-HTs showed many similarities with some variations. The synthesised Mg/Al-HTs, viz. $Mg_4Al_2(OH)_{12}CO_3.3H_2O$ and $Mg_6Al_2(OH)_{16}CO_3.4H_2O$, displayed the most superior stability properties, with the latter being the best PVC stabiliser, over the other HTs synthesised. The most important test conducted in this study, demonstrated the synthesised HTs ability to quench the HCl gas evolved as a result of dehydrochlorination, which occurs during the processing of PVC to useful polymeric products. Results from this study also confirmed that approximately 0.2 g of synthesised Mg/Al-HTs adsorbed 0.2 μmol of the HCl gas evolved, thus most effectively delayed the onset of degradation of powdered PVC (~10 g) than other HTs synthesised, including the non-stabilised PVC. It is thus evident that Mg/Al-HTs can function as effective heat stabilisers during the processing of PVC, with the potential of inhibiting the degradation of PVC, especially during the evolution of HCl gas.

Key words: Hydrotalcites, polyvinylchloride, thermal gravimetric analysis (TGA), dehydrochlorination, Brunauer–Emmett–Teller (BET) surface area, crystalline, amorphous.

INTRODUCTION

Lead compounds continue to assume an important role among stabilisers, especially in PVC derived products. Heat stabilisers are applied to polyvinylchloride (PVC) processing in order to prevent or minimise thermal instability, which is autocatalytic and leads to polymers adhering to the equipment (Gupta et al., 2008), discolouration, brittleness and insolubility. Common heat stabilisers used include metal salts, metal soaps and organometallic compounds. The toxicity and affinity for environmental pollution, renders these types of stabilisers harmful, therefore alternatives are required.

During the processing of PVC, stabilisers and additives are mixed and heated to form a solid, which can be subsequently moulded into a range of useful household and industrial products, examples: raincoats, toys, food packaging and conduits. When PVC is heated, chlorine and hydrogen atoms in the molecules are eliminated, and the release of HCl gas (dehydrochlorination) becomes apparent. This is an undesirable by-product that can negatively affect the properties and quality of the end products. Therefore it is vital that the evolution of hydrogen chloride be prevented, by using metal

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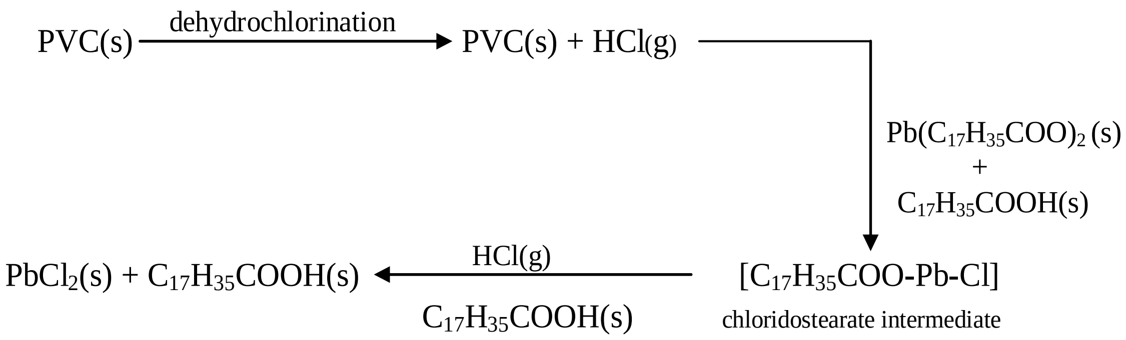


Scheme 1. Behaviour of lead stearate during the degradation of PVC.

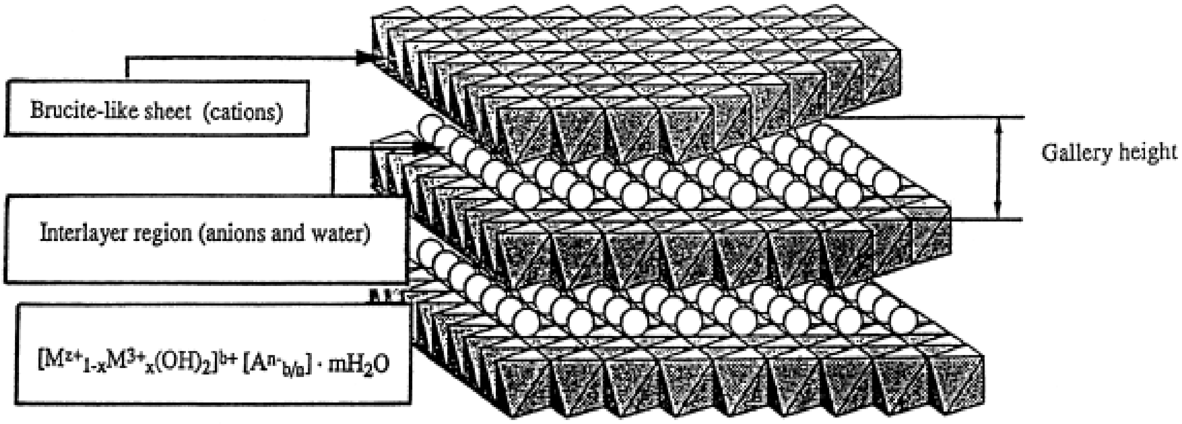


Figure 1. Layered structure of hydrotalcites with rhombohedral symmetry.

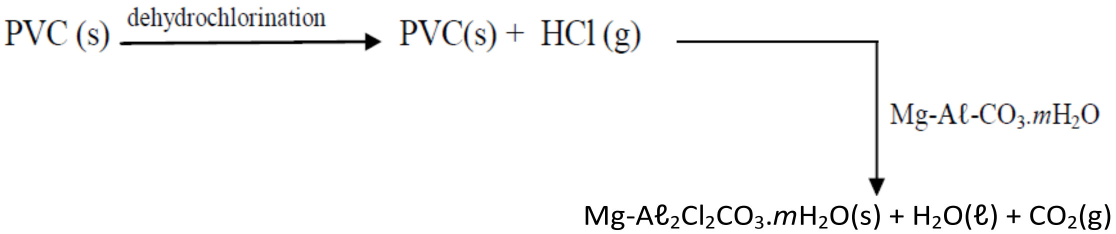
compound stabilisers.

A current additive, such as lead stearate [$Pb(C_{17}H_{35}COO)_2$], is used to quench the evolved HCl gas, which results in the formation of lead (II) chloride, as illustrated in Scheme 1, where lead chloridostearate was formed as an intermediate product and stearic acid served as a catalyst (Kalouskova et al., 2004). Lead stearate readily reacts with the evolved HCl gas and favourably affects the stability of PVC. However, the main concern is that the $PbCl_2$ formed as a product can leach into the environment as the polymer degrades. This is extremely harmful to the environment and the public because exposure to $PbCl_2$ is a common source of lead poisoning. This is another reason why alternatives need to be investigated. In this study, the use of hydrotalcites (HTs) as a lead replacement stabiliser in PVC processing was investigated. The general formula for HTs is represented by Equation 1, where M^{2+} and M^{3+} represent divalent and trivalent cations respectively (Morioka et al., 1995; Borja and Dutta, 1992; Lin et al., 2006; Yong and Rodrigues, 2002; Tong et al., 2011).

$$[M^{2+}_{1-x}M^{3+}_{x}(OH)_2](A^{n-})_{x/n} \, . \, mH_2O \qquad (1)$$

The synthesis of HTs involves the formation of positively charged (cations) layers and filling the interlayer region with anions. During this process, the initial solution contains carbonate and hydroxide ions. The metal ions are later added to this solution and bonds to the hydroxide ions to form the metal-hydroxide layers (indicated as ‘brucite-like sheet’ in Figure 1).

According to Gupta et al. (2008, 2009), the reaction between an Mg/Al-based HT and HCl gas is shown in Scheme 2. In comparison to lead stearate in Scheme 1, no harmful products are formed when an Mg/Al-HT reacts with the evolved HCl gas. This shows that HTs are more favourable (in terms of environmental health and safety) to use as stabilisers in the manufacturing of PVC polymeric products. In order to determine how HTs enhance the stability of PVC during degradation, synthesised HTs were used to quench HCl gas evolved as a result of thermal processing of PVC. Under conditions of elevated temperatures and UV radiation, PVC undergoes dehydrochlorination, where the evolved HCl gas is a polar covalently bonded gas. Signs of degradation during dehydrochlorination are apparent as severe discolouration of the PVC sample occurs. In this



Scheme 2. Behaviour of a Mg/Al-Hydrotalcite during the degradation of PVC.

study, results from the dehydrochlorination and thermogravimetric analysis performed on the PVC and HTs, will show that the synthesised HTs (as heat stabilisers) can inhibit the degradation of PVC by quenching the evolved HCl gas.

Lin et al. (2005) in Gupta et al. (2008), van der Ven et al. (2000) and Kalouskova et al. (2004) have also used HTs as heat stabilisers in PVC processing and suggested that a possible reason for its stabilising properties is due to ion exchange, where CO_3^{2-} ions are replaced by the absorbed Cl^- ions. Contrary to Lin et al. (2005) and Kalouskova et al. (2004) findings, Gupta et al. (2008, 2009) reported that besides ion exchange, adsorption of the evolved HCl gas by HTs is a major factor in the stabilisation of PVC.

The phenomena of adsorption can only be explained, according to Gupta et al. (2009), if the chloride ions on the surface of the HT are adsorbed, instead of exchanged with the carbonate ions. A possible mechanism for scavenging the evolved HCl gas using HTs was suggested by Gupta et al. (2008, 2009). Ion exchange is likely to occur if the chlorine atoms from the HCl are converted into Cl^- ions, however in the gaseous state this is least likely to occur. As a result, it is the surface adsorption of HCl gas onto the HTs that plays a significant role in heat stabilisation.

The research undertaken aims to explore the stabilising effect on PVC products during thermal processing using synthetic hydrotalcites.

MATERIALS AND METHODS

Synthesis of hydrotalcites

The metal solution, containing 0.75 M magnesium nitrate, zinc nitrate and/or aluminium nitrate, was transferred to the carbonate solution, containing 0.5 M sodium carbonate, using a burette at room temperature. This was conducted at a flow rate of ~1.0 mL/min under constant stirring. The pH was maintained between 11 and 12, by adding 2 M NaOH. Once the transfer was complete, the resulting mixture was stirred for 1.5 h at room temperature. The resulting metal/carbonate mixture was refluxed at 80°C, in an oil bath for 18 h, cooled to room temperature and filtered under a vacuum. The precipitate obtained was rinsed several times with deionised water and dried overnight at 110°C.

Characterisation

FT-IR spectroscopy

All FT-IR spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR Spectrometer with a universal ATR sampling accessory. The spectrum was recorded in the range of 4000-400 cm^{-1}.

Chemical analysis

To analyse the metal ions using ICP-OES, into a 50 mL centrifuge tube, 200 mg of each HT was accurately weighed and to it, 10 mL of aqua regia (3 parts HCl, 1 part HNO_3) was added. These tubes were sealed and placed on an orbital shaker for 2 h, centrifuged for 5 min then decanted into 100 ml volumetric flasks. The samples were filtered (by gravity) as it passed into the flasks and dilute to 100 mL with deionised water. These samples were prepared in triplicate and were analysed by a Perkin Elmer Optical Emission Spectrometer. The percentage of carbon, hydrogen and nitrogen present in the HTs was determined by accurately weighing approximately 2 mg of HT into a pre-shaped casing, closed and pressed into a pellet then analysed by a LECO CHNS-932 elemental analyser.

Physical analysis: PXRD, Surface area and pore volume

Powder X-Ray Diffraction (PXRD) studies was conducted on a Bruker AXS Diffraktometer D8, at room temperature, where a PXRD pattern with *d*-values was obtained using a scan range between 10 and 90° 2θ (theta) and a step width of 0.014°. The unit cell values were determined by the following equation:

$$\sin^2\theta = (\lambda^2/4a^2) \times N^{12} \qquad (2)$$

Determination of surface area and pore volume of the HTs was obtained using a Perkin Elmer instrument with Gemini 2375 V5.00 software.

Thermogravitmetric analysis

This analysis was performed by a SDT Q600 Thermogravimetric analyser, under nitrogen (100 mL/min) from 50 to 700°C at a heating rate of 10°C/min, where approximately 20 mg of sample was required. The HT and PVC powder were analysed individually, followed by the PVC-HT samples prepared by mixing 10 g of PVC powder and 200 mg of the synthesised HTs. From this analysis, a thermogram was obtained illustrating the sample's weight loss, derivative weight and heat flow as a function of temperature.

Dehydrochlorination

This is a thermal stabilising efficiency test, where the efficiency of the HT's ability to quench the evolved HCl was determined. Samples were placed in a round bottom flask and heated at 180°C in an oil bath, under a steady flow of nitrogen (60 mL/min). The HCl gas evolved was collected in a 100 mL Erlenmeyer flask, which was placed at the end of the condenser containing 50 ml of 4 μM NaOH solution with phenolphthalein indictor. The time taken for 0.2 μmol of HCl gas to evolve was recorded.

RESULTS AND DISCUSSION

The method for synthesising HTs is a well-established technique, and in this study the co-precipitation method was employed, which yielded a white precipitate in all cases. Our laboratory yields for all HTs ranging from 17 to 24% are considered low in comparison to yields recorded by others ranging from 80 to 90% (Mohan et al., 2005). According to Kloprogge et al. (2004a), HTs synthesised at pH 12 are more highly crystalline than the HTs synthesised at pH values other than 12. Thus, pH 12 was used as a standard bench mark for the synthesis of HTs in this study. However, according Vaccari et al. (1998), a pH range of 8-10 is also considered suitable for the synthesis of HTs. It is therefore possible that should a pH range of 8-10 be used, a higher yield of HTs would result, consequently, with a possible variation in the degree of crystallinity.

The use of FT-IR spectroscopy (generally used to identify the functional groups present in a HT structure composed of two or three metals) showed a broad band at ~3400 cm^{-1}, which is assigned to the stretching of the O-H bonds in the brucite-like sheets (Figure 1) in all six samples. However, a shift of this OH band to a higher wavenumber with increasing M^{2+}/M^{3+} ratios (HT 2 > HT 1 and HT 4 > HT 3) was observed. This is possibly due to a decrease in ionic radius across a period (from left to right) and an increase down a group (Zn^{2+} = 0.74 Å, Mg^{2+} = 0.65 Å, Al^{3+} = 0.50 Å). As a result, the electrostatic forces between Al^{3+} and OH^{-} (1:3) are stronger than that between Mg^{2+} or Zn^{2+} and OH^{-} (1:2). As the metal/hydroxide ion ratios decrease, less electrostatic forces are present, thus resulting in the hydroxide ions vibrating at higher wavenumbers.

As the number of metal ions in synthesised HTs were increased, the IR bands were observed at higher wavenumbers (Mg/Zn/Al-HT > Mg/Al-HT > Zn/Al-HT). Although Zn has a greater ionic radius than Mg, it is a transition metal with a completely filled d-orbital. Thus the electrostatic forces between Zn^{2+} and OH^{-} would be stronger than Mg^{2+} and OH^{-}, resulting in the O-H stretch of Zn-containing HTs vibrating at a slightly lower wavenumber than the initially observed 3400 cm^{-1}. The band observed at 3459.19 cm^{-1} was due to HT 5, which contained more Mg ions than Zn. All synthesised HTs showed two weak bands occurring as shoulders at ~2900-3000 cm^{-1} and ~1620 cm^{-1} respectively (as a result of the low percentage yields). The first according to Kloprogge and co-workers et al. (2004b) is due to the CO_3-H_2O bridging vibrations, and the second is assigned to the bending modes of H_2O caused by the hydrogen bonding between the molecules.

The carbonate ions found in the interlayer region of the HT structure shown in Figure 1 is indicative of a sharp intense band at ~1360 cm^{-1} due the antisymmetric stretching. For all synthesised HTs, three FT-IR bands were observed in the fingerprint region at ca. 550 cm^{-1}, ca. 630 cm^{-1} and ca. 770 m^{-1}. These bands are typically found in HTs and are due mainly to the lattice and translational vibrations of the metal ions, or the flexural vibrations of CO_3^{2-} (that is, 'rocking' of the molecule) (Seftel et al., 2005). A sharp band observed at approximately 440 cm^{-1}, is due to the lattice vibration of Al^{3+} which was observed in HT 1 and 6 only. Hence, it can be deduced that all relevant functional groups for example, CO_3^{2-} and OH^{-} are present in HTs synthesised. Also the addition of Zn to the Mg/Al-HT did not result in any major variation in the IR bands observed.

Table 1. Ratios of metals ions present in HTs synthesised determined by ICP-OES.

HT	Calculated ratios (Mg^{2+}:Zn^{2+}:Al^{3+})	Experimental ratios (Mg^{2+}:Zn^{2+}:Al^{3+})
1	4 : 0 : 2	4 : 0 : 2
2	6 : 0 : 2	6 : 0 : 2
3	0 : 4 : 2	0 : 5 : 1
4	0 : 6 : 2	0 : 7 : 1
5	4 : 2 : 2	4 : 3 : 1
6	2 : 4 : 2	2 : 5 : 1

The concentration of metal ions in HTs was determined from the relative intensities of metal ions using ICP-OES. The calculated and experimental values for the metal ion ratios in Mg/Al-HTs shown in Table 1 were found to be the same. However, laboratory synthesised Zn-containing HTs are found to contain one more Zn atom than the calculated amount. This results in one less Al atom being present in the Zn-containing HTs. It was suggested by Rajamathi et al. (2001) that Zn^{2+} ions occupy the tetrahedral as well octahedral sites in the layered structure. This can lead to competition between the Al^{3+} and Zn^{2+} ions for the tetrahedral sites in the structure.

From the C, H, N instrumental analysis, nitrogen, as expected, was absent in all HTs synthesised. This indicates that all nitrates were successfully removed from the precipitate during the washing stages using deionised water. Applying the general formula for HTs (Equation 1) theoretically and calculating it experimentally from C, H, N analysis, all synthesised HTs were found to contain one carbon atom. The variation of the number of hydrogen atoms in each HT, based on predicted and calculated results indicate that the amount of water

Table 2. Chemical formulae of synthesised HTs determined theoretically and experimentally.

HT	Calculated chemical formula	Actual chemical formula
1	$Mg_4Al_2(OH)_{12}CO_3.3H_2O$	$Mg_4Al_2(OH)_{12}CO_3.4H_2O$
2	$Mg_6Al_2(OH)_{16}CO_3.4H_2O$	$Mg_6Al_2(OH)_{16}CO_3.4.5H_2O$
3	$Zn_4Al_2(OH)_{12}CO_3.3H_2O$	$Zn_5Al(OH)_{12}CO_3.3H_2O$
4	$Zn_6Al_2(OH)_{16}CO_3.4H_2O$	$Zn_7Al(OH)_{16}CO_3.3.5H_2O$
5	$Mg_4Zn_2Al_2(OH)_{12}CO_3.3H_2O$	$Mg_4Zn_3Al(OH)_{12}CO_3.8H_2O$
6	$Mg_2Zn_4Al_2(OH)_{12}CO_3.3H_2O$	$Mg_2Zn_5Al(OH_{12}CO_3.6.5H_2O$

molecules in the interlayer region does not correlate to the expected values. Therefore from chemical analyses, the synthesised HTs were found to have an experimentally determined chemical formula (Table 2) that varied from the theoretically calculated formula.

In order to establish which HT that has the potential to function as an effective heat stabiliser for PVC, its physical properties needs to be investigated and considered. The crystalline or amorphous structural identification of HTs were investigated by PXRD (Figure 2a-f). In addition, the surface area and pore volume, from BET surface area analysis, is a direct indication of the synthesised HTs ability to quench the HCl gas.

According to Bastiani et al. (2004), broad and narrow symmetrical peaks observed in PXRD for HTs is a characteristic feature of a layered crystal structure HT. The PXRD patterns (Figure 2) obtained for all synthesised HTs in this study showed a similar trend thus confirming the formation of a layered crystal structure. The unit cell values calculated (Equation 2) for HTs synthesised in this study correlated to the literature value of 3.054 Å (Cavani et al., 1991). This confirms the rhombohedral symmetry in the layered structures of Mg/Al-HTs, with some variations in the Zn-containing HTs. The variations in the Zn-containing HTs may be attributed to a large cationic distance between Zn^{2+} ions. Consequently, the Zn-containing HTs were found to have a smaller pore volume than the Mg/Al-HTs, which was confirmed by BET surface area analysis (Table 3). Kloprogge et al. (2004) suggested that the higher the degree of crystallinity of the HT structure, the higher its thermal stability. However, the degree of crystallinity of the synthesised HTs using data obtained from PXRD patterns was uncertain.

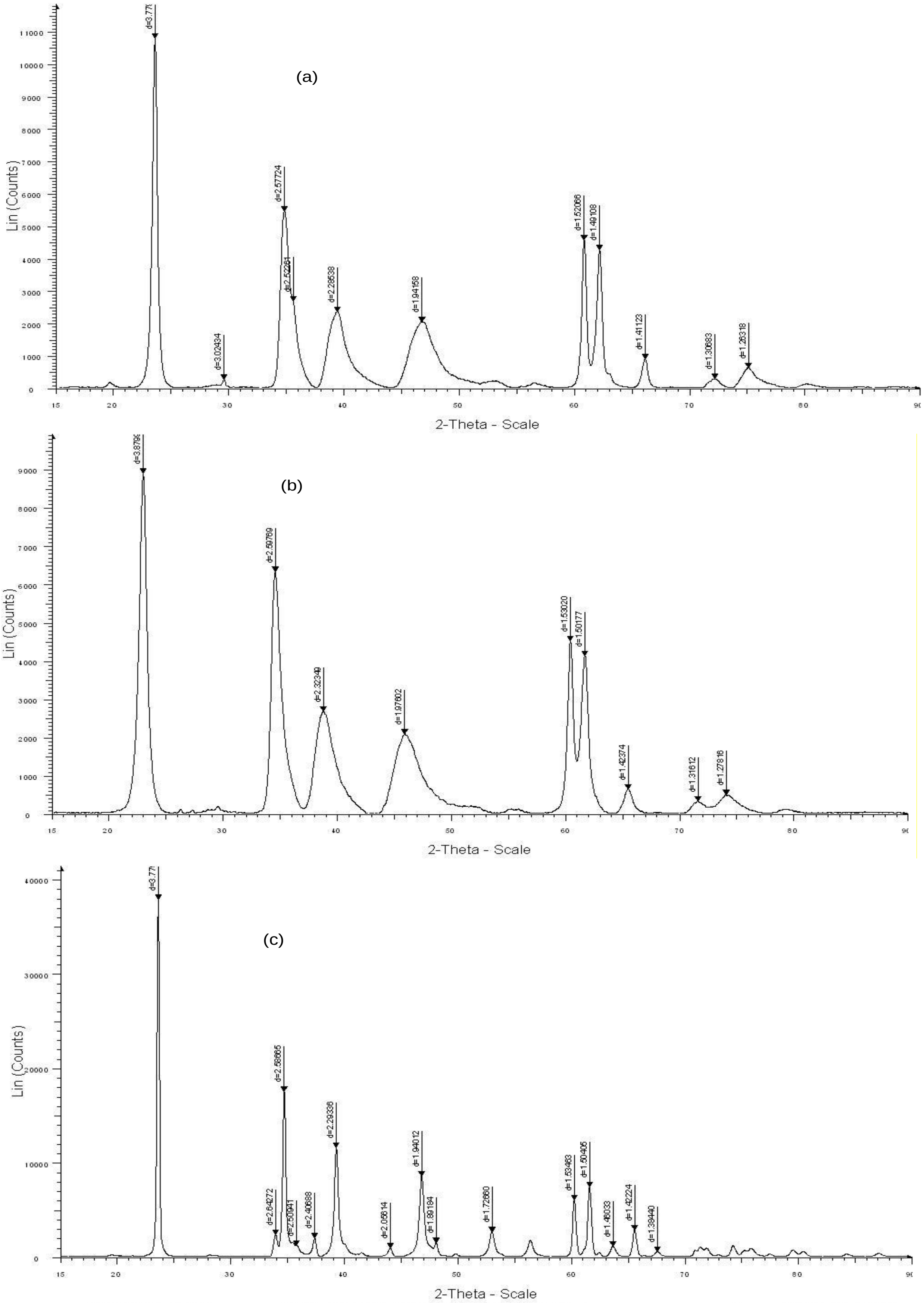
The Mg/Al-HTs were found to have a larger surface area and pore volume, in comparison to the other HTs synthesised. From the BET surface area results, it is observed that the surface area and pore volume of the Mg/Al-HTs are much larger than the Zn-containing HTs. This suggests that the Mg/Al-HTs can act as an effective adsorbent, which is consistent with its industrial applications, and would be an ideal heat stabiliser for PVC. Therefore from the physical properties investigated, the Mg/Al-HTs are most favourable to show an inhibition of the degradation of PVC during thermal gravimetric analysis (TGA) and dehydrochlorination.

From the TGA analysis, thermograms showed three distinct (temperature ranges 25-230°C, 230-450°C and 450-700°C) of weight loss. Since all synthesised HTs are highly crystalline (according to the PXRD results) and comprised of the same anions, any variation in the temperature range was therefore due to the different metal ion ratios. This was suggested by Rao et al. (2005) who indicated that HTs generally undergo two weight losses around 270 and 450°C, which depend qualitatively and quantitatively on many factors such as crystallinity, type of anions (Borja and Dutta, 1992), as well as nature and relative amounts of cations (Vaccari, 1998). Two sample weight losses are evidently present in the thermograms (Figure 3) for Mg/Al-HTs, verifying the formation of the layered structure illustrated in Figure 1. The thermograms for the Zn-containing HTs showed only one major loss in weight between 25-230°C, while PVC decomposed completely with two major weight losses between 230-500°C (Figure 4).

According to TGA-MS studies on HTs, the temperature at which the weight losses occur, suggest that the first weight loss corresponds to the loss of water molecules (Gupta et al., 2009; Lin et al., 2005; Mohan et al., 2005; Kloprogge et al., 2004a) present in the interlayer region. Upon further heating the second weight loss (subsequent to the first weight loss) involve dehydroxylation of the brucite-like sheets (Figure 1), as well as the removal of the carbonate anions as confirmed by Kloprogge et al. (2004a). The derivative weight loss curves for HTs 3, 4, 5 and 6, show only one major mass change, which resulted in a low total weight loss (reported in Table 4), as suggested by Cavani et al. (1991), who found that the carbonate ions can be removed from the interlayer without destroying the structure of the HTs.

Further results from TGA showed that HTs 1 and 2 were most stable compared to the rest of them. It was found that HTs 1 and 2 decomposed at 250 and 225°C respectively, while HTs 4 and 5 decomposed at lower temperature of 205°C. A higher thermal stability of HTs 1 and 2 is inherent arising out of their composition made up mainly of $Mg(OH)_2$ and $Al(OH)_3$ (which decompose at 350 and 300°C, respectively). As a result, the Mg/Al-HTs are mostly likely to be better heat stabilisers than Zn-containing HTs (comprising mainly of $Zn(OH)_2$ which decomposes at 125°C) (Cavani et al., 1991), as indicated by BET surface area analysis. Thermograms generated for HTs 1 and 2 were the only compounds which corresponded to data reported by Rao et al. (2005), Gupta et al. (2009), Lin et al. (2006) and Kloprogge et al. (2004) thus confirming high thermal stability over other HT's synthesised. Therefore based on derivative weight loss, HTs in order of increasing thermal stabilities are:

$$\text{HT } 4 \approx \text{HT } 5 < \text{HT } 3 < \text{HT } 6 < \text{HT } 2 < \text{HT } 1$$


(a)
Lin (Counts)
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
11000
d=3.77
d=3.02434
d=2.57724
d=2.52261
d=2.28538
d=1.94158
d=1.52066
d=1.49108
d=1.41123
d=1.30683
d=1.26318
15
20
30
40
50
60
70
80
2-Theta - Scale
(b)
Lin (Counts)
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
d=3.8799
d=2.59769
d=2.32349
d=1.97602
d=1.53020
d=1.50177
d=1.42374
d=1.31612
d=1.27816
15
20
30
40
50
60
70
80
2-Theta - Scale
(c)
Lin (Counts)
0
10000
20000
30000
40000
d=3.77
d=2.64272
d=2.58665
d=2.50941
d=2.40688
d=2.29336
d=2.05614
d=1.94012
d=1.89184
d=1.72660
d=1.53463
d=1.50406
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2-Theta - Scale

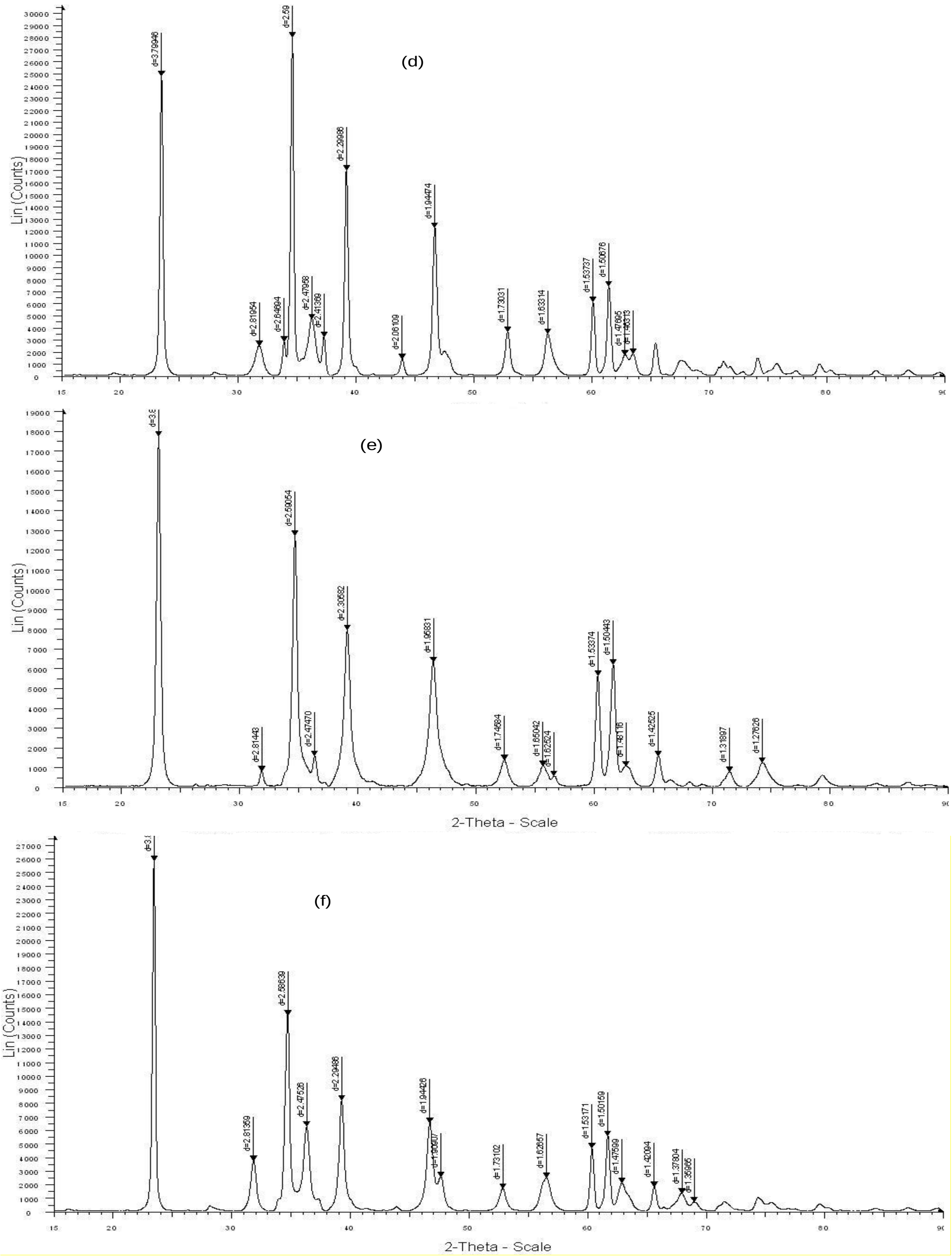

Figure 2. PXRD patterns obtained for HT's. (a) PXRD pattern obtained for $Mg_4Al_2(OH)_{12}CO_3.3H_2O$, (b) PXRD pattern obtained for $Mg_6Al_2(OH)_{16}CO_3.4H_2O$, (c) PXRD pattern obtained for $Zn_4Al_2(OH)_{12}CO_3.3H_2O$, (d) PXRD pattern obtained for $Zn_6Al_2(OH)_{16}CO_3.4H_2O$, (e) PXRD pattern obtained for $Mg_4Zn_2Al_2(OH)_{12}CO_3.3H_2O$, (f) PXRD pattern obtained for $Mg_2Zn_4Al_2(OH)_{12}CO_3.3H_2O$.

Table 3. Surface area and pore volume obtained for HTs synthesised.

HT	Sample mass	Surface area		Pore volume	
	/ mg	/ $m^2 g^{-1}$	/ m^2	/ $cm^3 g^{-1}$	/ dm^3
1	15.5	88.7000	1.375	0.5476	8.49
2	19.6	103.7092	2.033	0.5205	10.2
3	15.2	69.1270	1.051	0.0639	0.97
4	17.5	42.4833	0.743	0.1058	1.85
5	18.7	48.6898	0.910	0.2112	3.95
6	19.8	24.4649	0.484	0.0593	1.17

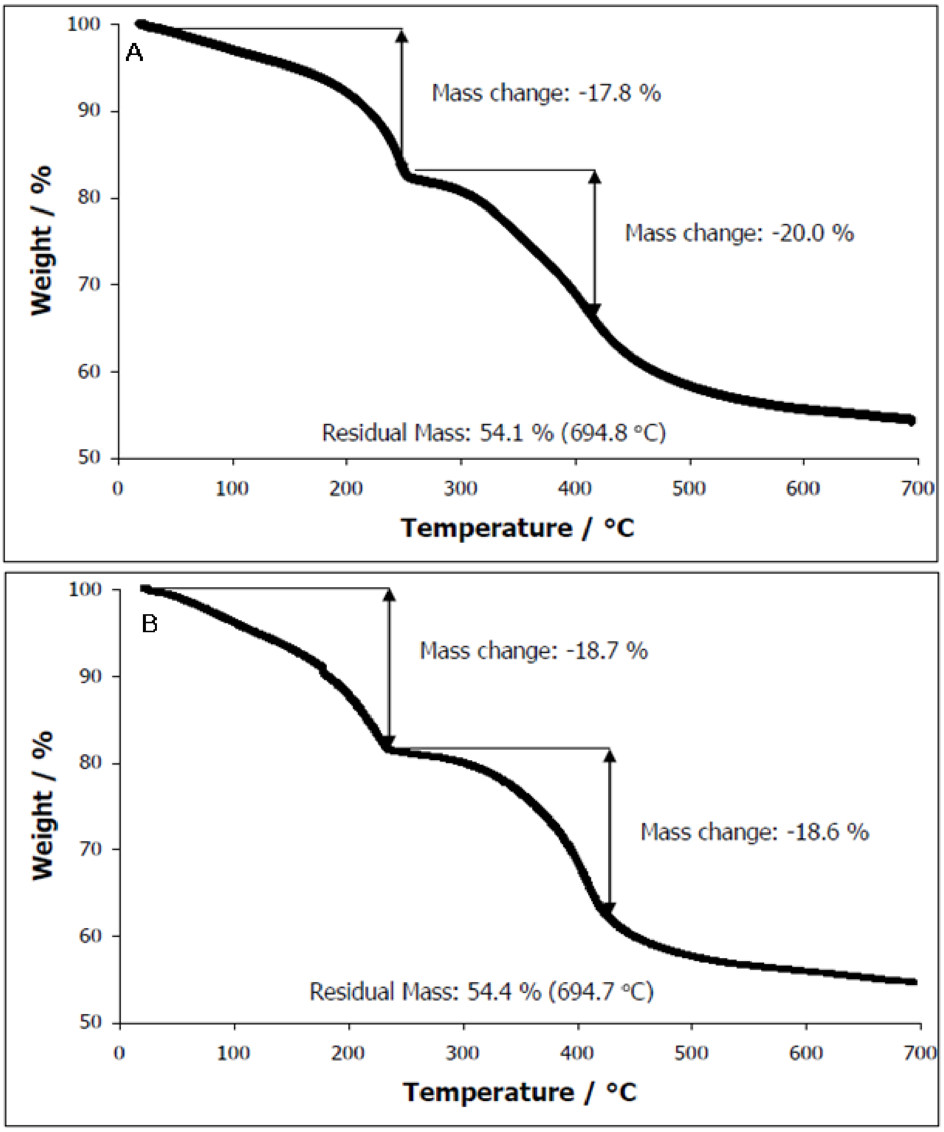

Figure 3. Thermograms for (A) Mg_4Al_2-HT and (B) Mg_6Al_2-HT.

Heating of the PVC powder, resulted in the evolution of HCl gas at temperatures greater than 180°C. From the thermogram for PVC (Figure 4), it was evident that the structure of PVC becomes unstable due to its facile

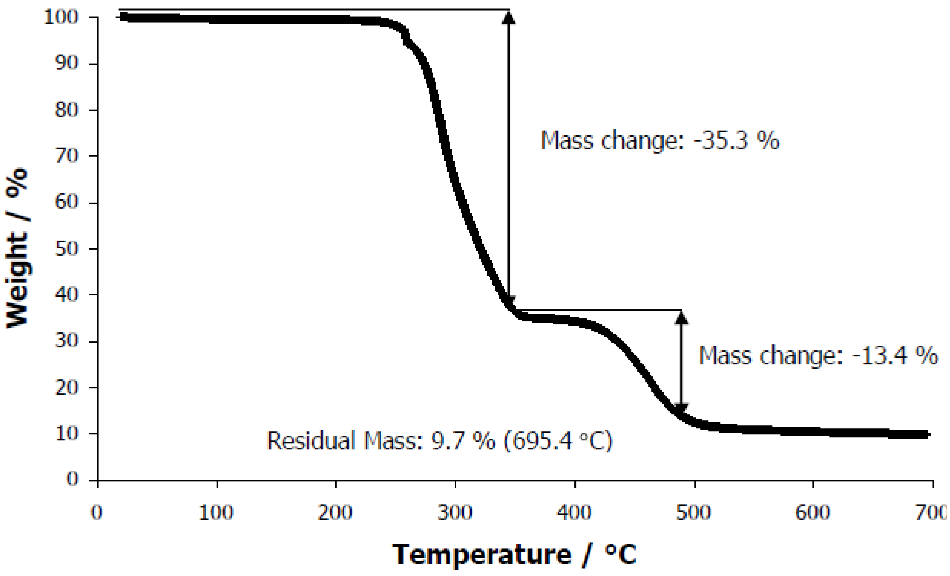

Figure 4. Thermogram for PVC.

Table 4. TGA data obtained for HTs and PVC.

Samples	Temperature / °C	Weight loss / %	Total weight loss / %
HT 1	250; 415	17.8; 20.0	45.9
HT 2	225; 415	18.7; 18.6	45.6
HT 3	215	18.0	33.0
HT 4	205	15.1	27.3
HT 5	205	15.0	37.6
HT 6	220	13.5	29.8
PVC	300; 460	35.3; 13.4	90.3

decomposition observed between 250-350°C. The process of dehydrochlorination (release of HCl gas from PVC) accelerates the degradation of PVC as observed from the continuous weight loss up to approximately 500°C. For this reason, heat stabilisers are an essential part of the PVC industry to prevent subsequent decomposition of the polymer upon heating. Potential inhibition of degradation of PVC by synthesised HTs is clearly evident from their characterisation using TGA, PXRD and BET surface area analysis. This can also be confirmed by the fact that at 700°C, all HTs maintained at least 50% of residual mass, indicating favourable thermal stability properties of the structure.

Since thermal stability is temperature dependant, the most stable synthesised HTs appear to be HT 4 and 6 showing lowest total weight loss (Table 4). However, the BET surface area results suggest that HTs 4 and 5 are most unlikely to quench the evolved HCl gas, due to its small pore volumes and surface areas. Although HT 4 and 6 show high thermal stability from the TGA results, it is the HTs ability to quench the HCl gas that is of importance to this study. Therefore from this analysis, it was observed that the HT thermal stability in increasing order is as follows:

HT 1 ≈ HT 2 < HT 5 < HT 3 < HT 6 < HT 4

The results of dehydrochlorination are reported in Table 4, where all samples were analysed under the same conditions. A blank analysis, containing PVC only, showed signs of degradation (decolourised to light brown) after 5 min. The Mg/Al-HTs (0.2 g) showed the highest thermal stabilisation by delaying the degradation of 10 g of PVC powder by 14 to 15 min in comparison to the blank analysis, where the PVC completely degraded after 12 min. Such results are consistent with the BET surface area results, where the Mg/Al-HTs had the largest surface areas and pore volumes. Therefore, the Mg/Al-HTs would be able to quench the most HCl gas in comparison to the other HTs synthesised.

PVC samples containing HTs 3 and 4 were the only samples to turn black after a short time, while all the other samples decolourised to light brown. This shows that Zn did not offer any stability towards the PVC, as the PVC-HT 6 sample degraded the fastest at 6.45 min. Therefore, the PVC samples containing HTs 3, 4 or 6 instability is consistent with the small surface area and pore volume observed. The time taken for the PVC samples containing HTs 3, 4 or 6 to degrade was less than the PVC containing no HTs. It can be suggested that the reason for the PVC samples containing HTs 3, 4 or 6 not being stable for at least 12 min was due to the extra Zn atom present in the HT, reported in Table 1.

Table 5. Adsorption rate of 0.2 μmol evolved HCl gas (dehydrochlorination) by HTs at 180°C.

Samples	Degradation Time/ mins	Observations
PVC (Blank)	12.00	Sample decolourised to light brown after 5 minutes.
PVC-HT 1	26.45	Sample decolourised partially from white to light brown.
PVC-HT 2	28.20	
PVC-HT 3	12.51	Sample turned black after 11 minutes.
PVC-HT 4	8.30	Sample turned black with fumes of HCl rapidly being given off after 8 minutes.
PVC-HT 5	12.42	Sample decolourised partially from white to light brown.
PVC-HT 6	6.45	

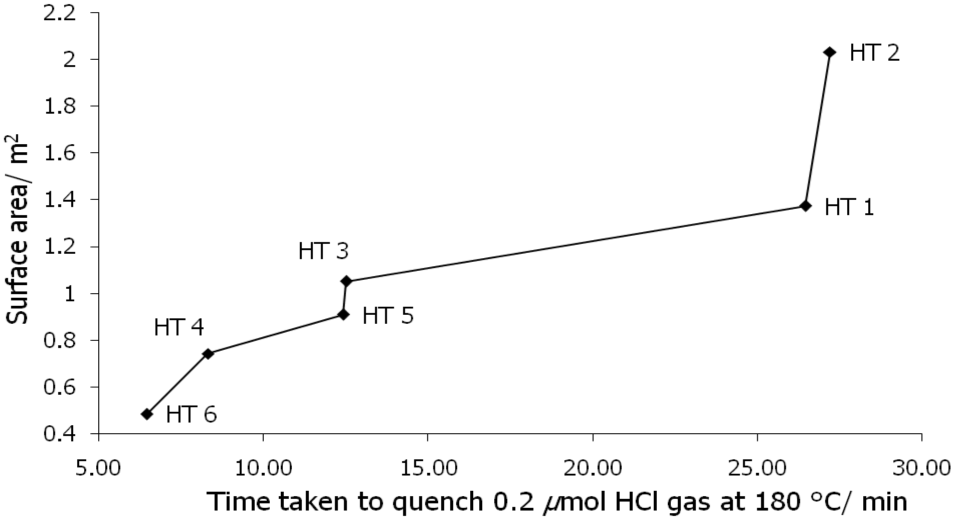

Figure 5. Correlation between the BET surface area and dehydrochlorination results obtained.

From the BET surface area and TGA results obtained, it is possible to assume that HT 3, 4, 5 and 6 did not form the expected layered structure and therefore a second weight loss was not observed on each thermogram recorded. Further investigation is deemed necessary to elucidate the structure of HTs 3, 4, 5 and 6. Although PVC-HT 5 has a small surface area and pore volume relative HTs 1 and 2, but larger than HTs 3, 4 or 6, showed signs of stabilising the PVC for approximately 42 seconds due to the presence of Mg in the HT. The observed thermal stability of synthesised HT from this analysis in order of increasing ability to stabilise the PVC is: HT 6 < HT 4 < HT 5 < HT 3 < HT 1 < HT 2.

It is also envisaged from the results obtained that the type of metal ions present in a synthesised HT has a significant effect on the thermal stability of PVC during dehydrochlorination as observed from the adsorption rate of evolved HCl gas shown in Table 5. This is confirmed by the relatively linear relationship between the HTs surface area and its ability to inhibit the degradation of PVC (Figure 5). Surface adsorption and not absorption, according to Figure 5, is the mechanism in which Mg/Al-HTs quench evolved HCl gas. Stabilisation of PVC by HT 3 was more effective than HT 4 due to its surface area rather than to its pore volume. HT 2 was found to have the largest surface area over all synthesised HTs and consequently was the most effective in stabilising the PVC powder. HT 6 was found to have the smallest surface area and as a result, did not stabilise the PVC at all. Hence from the HTs synthesised in this study, HT 2 ($Mg_6Al_2(OH)_{16}CO_3.4H_2O$) has proven to be the most effective heat stabiliser in processing of PVC to useful polymeric products.

Conclusion

The results from this study show that Mg/Al-HTs have proven to potentially function as ideal heat stabilisers in processed PVC products. From the PXRD studies, it can be confirmed that the Mg/Al-HTs synthesised in this study were the only HTs which formed layered structures with rhombohedral symmetry. A combination of favourable properties, such as a large surface area confirmed by the BET surface area analysis, thermal stability and quenching ability of a PVC-HT blend determines the inhibition potential of dehydrochlorination. The addition of Zn to the Mg/Al-HT did not benefit the HT and in fact accelerated the degradation of PVC during dehydrochlorination. Mg/Al-HTs were able to adsorb 0.2 μmol of HCl gas evolved during the degradation of PVC and significantly delayed the onset of degradation of PVC relative to the other HTs synthesised, including the non-stabilised PVC sample. Therefore scavenging of HCl gas by synthesised Mg/Al-HTs in this study has shown an increase toward the inhibition of degradation and thermal stability of PVC during its processing.

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